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FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

STUDY OF GRAPHENE AS ELECTROCATALYST SUPPORT FOR HIGH TEMPERATURE POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

GONÇALO DE ALMEIDA BARRETO DA COSTA MONTEIRO

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GONÇALO DE ALMEIDA BARRETO DA COSTA MONTEIRO

Dissertation presented to obtain the degree of

MASTER IN ENVIRONMENTAL ENGINEERING

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“It is paradoxical, yet true, to say, that the more we know, the more ignorant we become in the absolute sense, for it is only through enlightenment that we become conscious of our limitations. Precisely one of the most gratifying results of intellectual evolution is the continuous opening up of new and greater prospects.”

Nikola Tesla

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A muitos tenho de agradecer, não apenas por este semestre, mas sim pelos 5 anos mais fantásticos que tive.

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Obrigado a todos!

ABSTRACT

Fuel cells (FC) consist in electrochemical systems that convert chemical energy of a fuel into electricity and present a very auspicious technology since it provides high efficiencies and low or zero emissions. FC use platinum as a catalyst which promotes high efficiencies, however it is expensive, being an obstacle to a wider application. Graphene has been studied in several purposes due to very interesting properties, like the high electric conductivity. So, in the current work, graphene is studied as a catalyst support for High Temperature PEMFC (HT-PEMFC), promoting the electrocatalyst activity. The study performed involved several stages, starting with the oxidation process (Tours' and Hummers' method) of graphite and graphene. The material produced as well as commercial samples were used in platinum chemical deposition process. Targeting a 20% platinum deposition, this was deposited in the carbon surfaces with a known procedure in LEPABE. Finally, electrodes were produced by spraying the developed materials into a gas diffusion layer. Several characterization techniques were used. The graphene oxide and reduced graphene oxide supported platinum were analysed by thermogravimetric analysis (TGA), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and field emission scanning electron microscopy (FE-SEM). Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were used to analyse the electrodes. TGA curves provide knowledge of the amount of platinum deposited. A MEA was assembled with an electrode produced (GO 1:3 with modified Hummers' method and a membrane from Advent) and tested at 160ºC. Graphene oxide with different oxidation degrees was obtained and platinum was successfully deposited in several supports, including graphene or reduced graphene oxide. TGA experiments show that residual oxygenated groups are present in most of the samples after platinum deposition. The electrocatalyst supported in reduced graphene oxide (obtained with Hummers' method) show that a higher oxidation degree in graphene oxide originated higher dispersion of platinum and with smaller size. However, the obtained platinum particles in the supports have a higher size than the commercially available platinum supported in carbon black. Cyclic voltammetry analysis of the produced electrodes show that the hydrogen associated peaks are less visible for samples produced with more oxidized graphene oxide. The Tours' method originated electrodes with more defined peaks when compared to the modified Hummers' method, suggesting a higher electrochemically surface area. The CV operational conditions and set up were developed and optimized. The MEA produced showed a very low performance. The Nyquist plot indicated very high ohmic and electrodes resistances. The amount of phosphoric acid in the membrane was not optimized as well as the production of electrodes, reducing drastically the MEA performance. The main objective of the project was accomplished, but more work is yet to be developed to fully evaluate graphene as a platinum support in HT-PEMFC.

KEYWORDS: Platinum, Chemical deposition, Graphene, HT-PEMFC, Cyclic Voltammetry, Thermogravimetric Analysis, Electrochemical Impedance Spectroscopy

RESUMO

As células de combustível consistem em sistemas eletroquímicos capazes de converter energia química de um combustível em electricidade, promovendo altas eficiências e emissões quase nulas. As células de combustível usam platina como catalizador, a qual promove elevadas eficiências referidas, contudo tem um preço considerável, sendo um obstáculo a aplicações mais gerais. O grafeno tem sido estudado com diversos fins uma vez que apresenta vantagens promissoras, como a alta condutividade elétrica. Assim, neste trabalho, o grafeno é estudado como um suporte de catalizador das células combustíveis de permuta protónica de temperatura elevada promovendo a atividade eletrocatalítica. O estudo desenvolvido envolve várias etapas, começando com o processo de oxidação (métodos de Tour e de Hummer) de grafite e grafeno. O material produzido, assim como amostras comerciais, foram usados na deposição química de platina. Objetivando-se 20% de deposição de platina, esta foi depositada na superfície das amostras com um procedimento já conhecido no LEPABE. Finalmente, elétrodos foram produzidos através de deposição dos materiais obtidos num camada difusiva. Várias metodologias de caracterização foram feitas, desde análise termogravimétrica (TGA), inductively coupled plasma-atomic emission spectrometry (ICP-AES) e field emission scanning electron microscopy (FE-SEM). Voltametria cíclica e espectroscopia de impedância electroquímica foram usadas para analisar os elétrodos. As curvas de TGA obtidas permitiram prever a quantidade de platina depositada. Uma MEA foi feita com um elétrodo produzido (GO 1:3 com método de Hummer modificado) e testada a 160ºC. Grafeno oxidado com diferentes graus de oxidação foi obtido e a platina foi depositada com sucesso em diversos suportes.

As curvas de TGA indicam grupos oxigenados residuais presentes na maioria das amostras, após a deposição de platina. O eletrocatalizador suportado em grafeno oxidado reduzido (obtido com grafeno oxidado com o método de Hummer modificado) indica que um maior grau de oxidação no GO origina uma maior dispersão e menor tamanho de partícula de platina. Contudo, as partículas de platina obtidas nos suportes têm um maior tamanho que as obtidas com as amostras comerciais (em Carbon Black). A análise através de voltametria cíclica dos elétrodos produzidos indica que os picos associados às reações do hidrogénio são menos visíveis para amostras produzidas com grafeno oxidado com mais $KMnO_4$. O método de Tour origina elétrodos com curvas mais definidas quando comparado com os elétrodos preparados com o método de Hummer, indicando uma maior ECSA. As condições de operação de um CV foram otimizadas. A MEA produzida apresenta um desempenho muito baixo (o valor máximo de corrente obtida foi de 10.2 mA) e o Diagrama de Nyquist indica resistências ómicas e dos elétrodos muito elevadas. A quantidade de H_3PO_4 na membrana não foi otimizada, assim como a produção de elétrodos, reduzindo o desempenho da MEA. O principal objetivo do trabalho foi atingido, mas mais trabalho é necessário.

PALAVRAS-CHAVE: Platina, Deposição Química, Grafeno, HT-PEMFC, Voltametria Cíclica, Análise Termogravimetrica, Espectroscopia de Impedância Electroquímica

I declare, under oath, that this work is original and that all non-original contributions were properly referenced with identifying the source.

Gonçalo de Almeida Barreto da Costa Monteiro

Porto, 23 de julho de 2015

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NOMENCLATURE

VARIABLES

Variable	Definition	Unit
ECSA	Electrochemical surface area	cm^2_{Pt}/g_{Pt}
f	Frequency	Hz
i	Current	A
j	Current density	mA/cm^2
L	Platinum Loading	$g_{Pt}/cm^2_{electrode}$
pH	Ionic Hydrogen Potential	pH scale
q_{Pt}	charge density	C/cm^2electrode
V	Potential	V
Z	Impedance	$\Omega.cm^2$
Z''	Imaginary Impedance	$\Omega.cm^2$
Z'	Real Impedance	$\Omega.cm^2$

GREEK SYMBOLS

Greek Symbol	Definition	Unit
θ	Phase angle	degree
Γ	charged needed to reduce a monolayer of protons on Pt	$\mu C/cm^2_{Pt}$

UPPERSCRIPTS

Upperscripts	Definition
º	Standard
e^-	Electrons

SUBSCRIPTS

Subscripts	Definition
Z_Ω	Ohmic Resistance
Z_{fA}	resistance associated with the anode
Z_{fC}	resistance associated with the cathode

ABBREVIATIONS

Abbreviation	Definition
AFC	Alkaline Fuel Cell
CE	Counter electrode
CV	Cyclic Voltamogram
EU	European Union
EG	Ethylene Glycol
EIS	Electrochemical Impedance Spectroscopy
FC	Fuel Cell
FE-SEM	Field Emission Scanning Electron Microscopy
H5	Commercial Graphene H5
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
M5	Commercial Graphene M5
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assemble
HAD	Hydrogen adsorption/desorption reactions
HT-PEMFC	High Temperature Polymer Electrolyte Membrane Fuel Cell
Hummers'	Modified Hummers' method
LEPABE	Laboratory for Process Engineering, Environment, Biotechnology and Energy
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
Pt	Platinum
RE	Reference electrode
RPM	Rotations Per Minute
SOFC	Solid-oxide Fuel Cell
Sigracet 10 CC	10597 GDE Sigracet 10CC with 0,5 mg Pt/cm^2
TGA	Thermogravimetric Analysis
Tours'	Tours' method
WE	Working electrode
TPS	Commercial membrane by Advent

1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

The evolution of societies is closely followed by a consumption of natural resources to a considerable amount of ends, like energy demands, food, technology, etc. For instance, presently, three quarters of the energy consumption in the European Union are based on fossil fuels – nonrenewable sources of energy, Figure 1 [2].

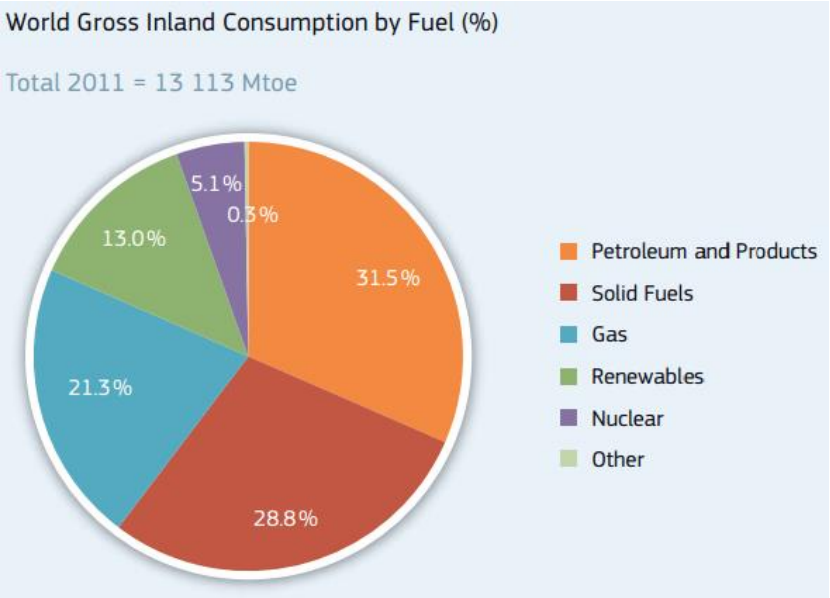


***Figure 1** - World Gross Inland Energy Consumption by Fuel in 2011[3].*

Taking this into account, the EU has created the Renewable Energy Directive, which establishes a general ruling for the production and promotion of energy from renewable sources. To reach this goal, at least 20% of the EU energy needs must be derived from renewables by 2020. At the same time, every member of the EU needs to ensure that a minimum of 10% of their transport fuels are provided by renewable sources by 2020 [4].

Fuel cells have been studied for years and present a very promising energy technology since they provide high efficiencies with low or zero emissions [5]. Hydrogen is an energy carrier and is a common fuel used in fuel cells. It can be stored and produced by clean methods that provide a great link between sustainable energy technologies and energy consumption, which is commonly reported as the hydrogen economy [6]. A wider use of fuel cells can promote the hydrogen economy.

In particular, Polymer Electrolyte Membrane Fuel Cells (PEMFC) have been considered for small stationary applications and as alternative to internal combustion engines, for transport applications. This type of fuel cells usually uses platinum or bimetallic catalysts (like

platinum/ruthenium) as catalyst. Commonly, the electrocatalyst is supported in nano sized carbon materials, increasing active area and decreasing the amount of platinum needed to carry out the electrocatalyst reactions [7, 8]. Carbon black (CB) is the most used platinum support for HT-PEMFC catalysts [9]. This material presents a high electrical conductivity, great surface area and a relatively low cost. However, also presents some disadvantages that includes high amount of micropores and the morphological changes under extensive fuel cell use. As a consequence, catalyst sintering or detachment from the support may occur [10].

To avoid the disadvantages related to CB use, other nanostructured carbon materials, such carbon nanotubes (CNTs), carbon nanohorns (CNHs), carbon nanocoils (CNCs) and carbon nanofibers (CNFs), are being studied due to their suitable porosity, custom-made morphology and good electrical and mechanical properties [7].

Graphene presents 2D crystals and has excellent thermal and electric conductivity and high mechanical strength [11, 12].

1.2 OBJECTIVES OF THIS WORK

In the current work, graphene is studied as a catalyst support for High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFC).

It is planned the preparation of electrodes with electrocatalysts based on platinum supported in graphene and carbon black. To obtain these electrodes several work stages must be performed: production of oxidized graphene, preparation of graphene oxide and graphene supported electrocatalysts, characterization of prepared materials (thermogravimetric analysis (TGA), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and field emission scanning electron microscopy (FE-SEM)), preparation and characterization of the electrodes (Cyclic Voltammetry) and finally the preparation and characterization of membrane electrode assembly in a fuel cell set-up (Electrochemical Impedance Spectroscopy).

The current work is framed within the project Flexible glass-based proton exchange membrane and MEA for high temperature PEMFC (FCT – Cooperation Agreement between Portugal and China).

1.3 LABORATORY PRESENTATION

The work developed was performed in LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy – in the Faculty of Engineering of the University of Porto. LEPABE is a research unit from the national network of R&D units, accredited by FCT,

and consecutively rated as "Excellent" by the international committees appointed by FCT. Research activities aim at obtaining advances in science and use these to support the development of innovative processes and products.

The main areas of research are environmental, chemical and biological engineering with three defined goals: environment and health; energy, processes and products; biotechnology and interfaces. The multidisciplinary of the LEPABE has proven to be an important tool to achieve the goals mentioned and this is only possible by the hard work of 22 researchers and 75 students from multiple areas of studies.

LEPABE's areas of research are important to sustainability, since it focuses on innovative materials, new energy processes and many other that might be important to achieve a stable environmental and economically civilization. In the end the laboratory's work permits a combination of scientific development with technological applications, which have been the base to a number of patents accepted. This results in considerable collaborations with companies and institutions in fields like polymers, paint technology, water, food processing and many others.

1.4 CONTRIBUTIONS OF THIS WORK

The current work is framed within the project Flexible glass-based proton exchange membrane and MEA for high temperature PEMFC (FCT – Cooperation Agreement between Portugal and China). To the knowledge of the author, graphene has not been previously used as catalyst support for high temperature polymer electrolyte fuel cells (HT-PEMFC). Since graphene is being used as the first time as electrocatalyst support for HT-PEMFC in LEPABE, an extensive work was performed regarding the electrodes characterization, especially on cyclic voltammetry characterization.

1.5 THESIS' ORGANIZATION

The present work is organized in 5 different chapters. The first chapter introduces the objectives and a framework of the project. Furthermore, a presentation of the laboratory where the work was developed is made in order to complete an overall idea of the study. In the second chapter, it is presented the state of the art of this work, in which a theoretical overview of the relevant subjects is made, considering the PEMFC, electrode preparations and several characterization techniques. The third chapter includes the description of the procedures elaborated and equipment used. In the fourth chapter, the results obtained are presented and an evaluation is made. Finally, in the fifth chapter, conclusions are presented

in order to know if the objectives presented were fulfilled. To complement the project and pursue a more fund idea, some suggestions to future works are indicated in the end.

2 STATE OF THE ART

2.1 FUEL CELLS

Fuel cells are devices that continuously convert chemical energy provided by a fuel and an oxidant, into electricity, without combustion. Water and heat are resulted from this process [13, 14]. Fuel cells possess two electrodes, cathode and anode, with an electrolyte between them [14]. Figure 2 shows the simplest example, in which hydrogen is the fuel and oxygen the oxidant.

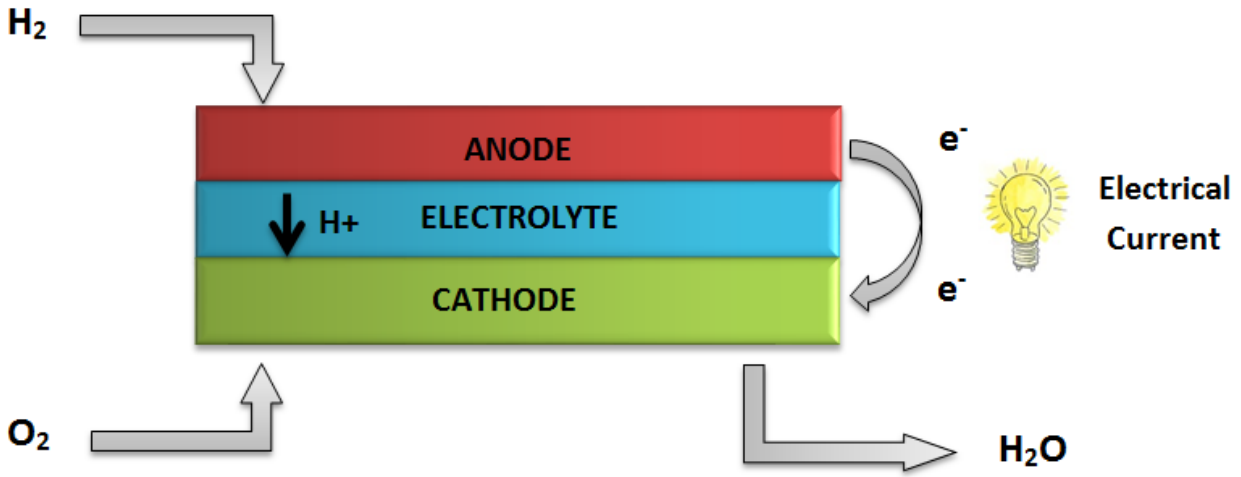


***Figure 2** - Diagram of a Fuel Cell overall process.*

Hydrogen is the most common fuel used in fuel cells. This is fed at the anode and reacts catalytically, splitting into protons and electrons [5].

The electrolyte allows the passage of protons, but prevents electrons that straddle over an external circuit. Oxygen is fed at the cathode and reacts with the protons that cross the membrane and the electrons coming from the external circuit. This reaction originates water Thus, hydrogen is oxidized at the anode and oxygen is reduced at the cathode [15].

Compared with fuel cells, batteries provide potentially lower energy densities and can't be used continuously, since it demands recharge. This last issue does not affect fuel cells, since it can be used non-stop, as long as the fuel is provided. Additionally, compared to an internal combustion engine, fuel cell systems have higher energy conversion efficiency [13].

There are different types of fuel cells, classified accordingly to their electrolyte. The most mentioned types in the literature are:

- Phosphoric Acid Fuel Cell (PAFC)
- Alkaline Fuel Cell (AFC)
- Polymer Electrolyte Membrane Fuel Cell (PEMFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid-oxide Fuel Cell (SOFC)

Figure 3 shows the mechanisms of each type of fuel cell.

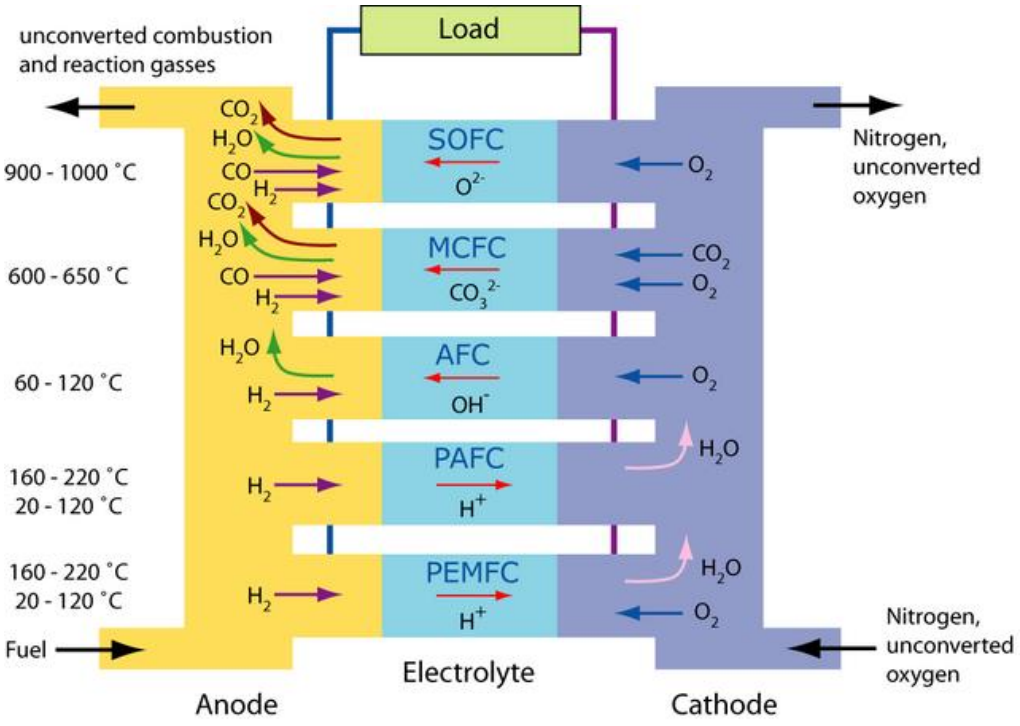


***Figure 3** – Working mechanisms, temperature range, fuels and products of various types of fuel cells: SOFC, MCFC, AFC, PAFC and PEMFC [16].*

A short description is presented below.

1. PAFC uses phosphoric acid (H_3PO_4) as the electrolyte, in which protons (H^+) pass through. These systems operate at, approximately, 200ºC and present relatively low efficiencies (near 55%) when compared to the other fuel cells;
2. Alkaline fuel cells use sodium hydroxide (NaOH) or potassium hydroxide solution (KOH) as electrolyte and works between 60ºC and 120ºC. In this case, hydroxyl ions (OH^-) are transported through the electrolyte;
3. MCFC operate at really high temperatures, achieving values between 600ºC and 700ºC. Molten carbonate cells present high working efficiencies of 65% and use as

electrolyte molten alkali carbonate liquids, which potentiate the passage of carbonate ions (CO_3^{2-});

4. SOFC are the cells able to work at the higher temperatures, achieving 1000ºC and reaches 65% of efficiency. Electrolyte in an SOFC consists in a solid ceramic-based material like yttrium-stabilized zirconium. In SOFC, MCFC and AFC the ion movement is from the cathode to the anode, while in PAFC and PEMFC the ions cross in the opposite direction.
5. PEMFCs use a thin polymer membrane as an electrolyte, with platinum as the most common catalyst, frequently supported on a carbon material. Protons are the ionic charge carrier in membrane [14]. PEMFC usually work at low temperatures (below 90ºC) and might be vastly used in the future in cars and portable power applications, for example [5, 13, 17]. PEMFC will be described in more detail forwardly.

Different fuels, like pure hydrogen, reformate hydrogen or even methanol or natural gas can be used as fuel, depending on the fuel cell type. To sustain a vast use of hydrogen as fuel, it is important to develop better storage and transport capabilities [6].

2.2 Brief History of the Fuel Cells

The operating principle related to the fuel cells was revealed by Sir William Grove in 1939, which called it the “gaseous voltaic battery”, while Christian Schönbein made an identical discovery at about the same time. Figure 4 presents the system developed by Grove, not experimentally tested, however. Roughly one century after, Francis Bacon worked on a practical approach of a fuel cell, developing a 6 kW cell by the end of 1950s.

The first big application of a fuel cell was in the United States Space Program, during the Gemini Program in the early 1960s, and in the Apollo Space Program, to produce electricity for life support, communications and guidance (PAFC). In the same decade, General Motors used fuel cells to power a van [5]. In the 1990s a considerable amount of progress has been achieved regarding fuel cells, resulting in the development of a fuel cell powered submarine (1989), buses and cars with these systems (1993). From this point on the number of fuel cell-related patents grown significantly, especially in Japan and U.S.A. [5].

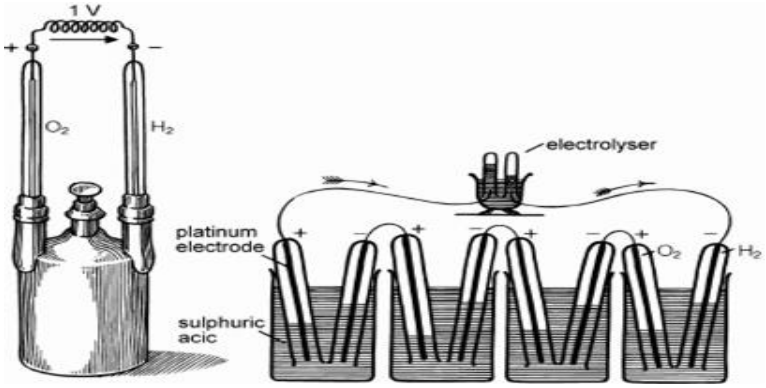


Figure 4 *– Representation of the Fuel Cell principle developed by Sir William Grove in 1839. [18]*

2.3 PEMFC

PEMFC possess a thin polymer electrolyte membrane between anode and cathode, with a typical thickness between 20-200 μm [13, 14]. This assembly is usually called membrane electrode assemble (MEA) [15]. Figure 5 presents a schematic of a typical PEMFC.

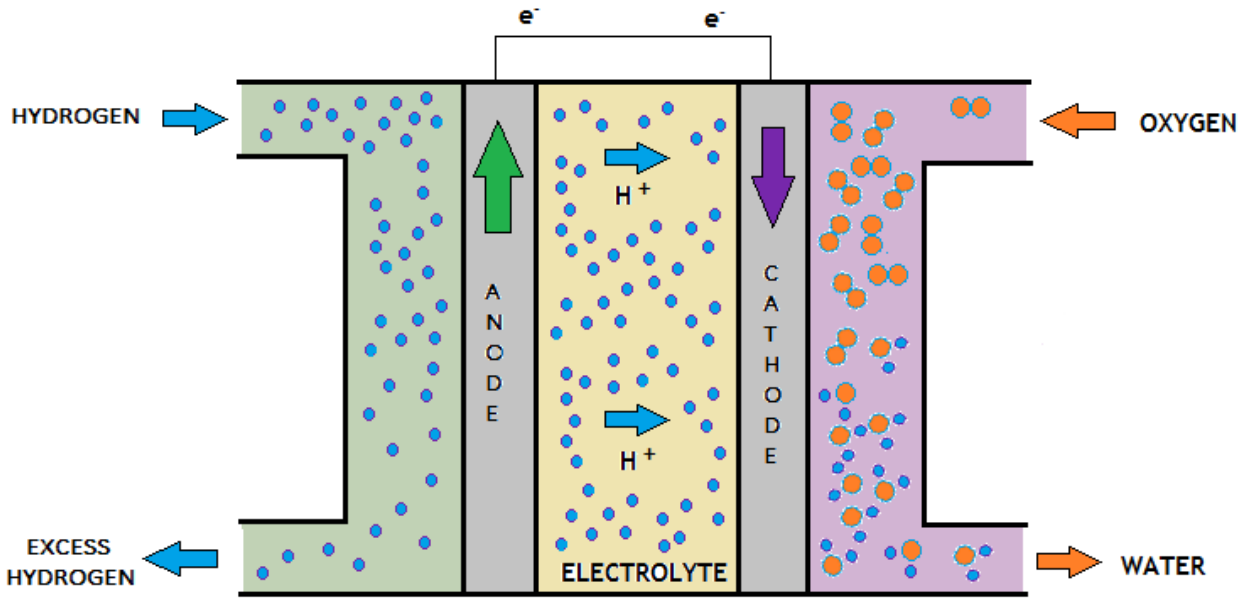


Figure 5 *– Presentation of electrochemical processes in a PEMFC.*

The electrodes are composed of a gas diffusion layer (GDL) and a catalyst layer. The GDL, usually carbon paper or carbon cloth [15], ensures that reactants diffuse properly to the catalyst layer. Additionally to this property, GDL must be the electrical conductor, transporting electrons to and from the catalyst layer [14, 15]. This layer, either applied to the gas diffusion layer (GDL) or the membrane is usually platinum supported in a carbon material. The catalyst layer is in contact with the GDL and with the membrane. Platinum-loaded carbons are usually mixed with Nafion solution and coated with PTFE (Teflon) in order to increase proton conductivity and prevent flooding [15, 19]. The typical membrane used in

PEMFC is Nafion® type membranes. They provide high proton transport, but only when well humidified. A MEA is produced by pressing together gas diffusion layer, catalyst layers and membrane [15].

PEMFC normally operate at temperatures below 90ºC due to the type of membrane used, which presents high conductivity only under highly humidified conditions. At temperatures lower 90ºC, water presents a dual-phase system that can promote a starvation at the anode, dehydration of the membrane and flooding at the cathode. By comparison, the operation at higher temperatures present several advantages, like enhancement of electrochemical kinetics, the simplification of the cooling system, increase of the CO tolerance (allows to use lower quality reformed hydrogen) and help to mitigate issues related to water management. [17, 20]. This is why High Temperature PEMFC have been in center of many research groups. The MEA of HT-PEMFC is based on polybenzimidazole/phosphoric acid (PBI/H_3PO_4) electrolyte or on pyridine based aromatic polyether/phosphoric acid (PPE/H_3PO_4) electrolyte (Advent Technologies). Phosphoric acid has a low vapor pressure at high temperatures and considerable proton conductivity [17].

Platinum group metals are known for their catalytic activities for a vast number of chemical reactions and can be deposited in supporting surfaces [21]. Platinum is the most usual catalyst in PEMFC, used in both the cathode and anode, which is commonly supported by carbon with a considerably high surface area. It is worth mentioning that extensive research endorsed the reduction of the platinum loading, since 4 mg/cm^2 to 0,4 mg/cm^2. This allowed to dramatically lower the total cost involved [15, 22]. It is known that catalytic activity of metals depends on the size, shape and distribution of the metal particles. Particles with smaller sizes are wanted for PEMFC electrodes, since they promote the surface area to reduce hydrogen. The dissociative electrosorption of molecular hydrogen followed by facile electron transfer with platinum react as follow [23].

$$H_2 + 2Pt \leftrightarrow 2Pt - H_{ads}$$
$$2Pt - H_{ads} \leftrightarrow 2Pt + 2H^+ + 2e^-$$

Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) has been used as platinum precursor supported in different carbonaceous materials [23]. This solution is the most widely used and promotes a good platinum deposition on carbon surfaces [10]. It allows obtaining small platinum particles. Kim et al. [24] obtained 1.6-3.4 nm using H_2PtCl_6 as precursor and Ismagilov et al. recovered 3.2-5 nm particle size range [23].

2.4 PEMFC ELECTRODES PREPARATION

Platinum is deposited onto the support, using Pt precursors and a reducing agent like ethylene glycol (EG).

Carbon-type materials are most commonly used as platinum supports in fuel cells. Carbon is used since it presents a vast number of advantages that could promote the efficiency of the system, like an acid/base resistant structure or its resistance to high temperatures and high electronic conductivity. The surface of carbon materials can be modified in order to increase the electrocatalyst deposition. It was verified that, by reducing the hydrophobicity of the carbon by increasing the amount of oxygenated groups, the surface was more accessible to the aqueous solution of the metal precursor during impregnation. These groups might be developed by changes in the solution (pH or temperature) or by processes of oxidation [15, 25].

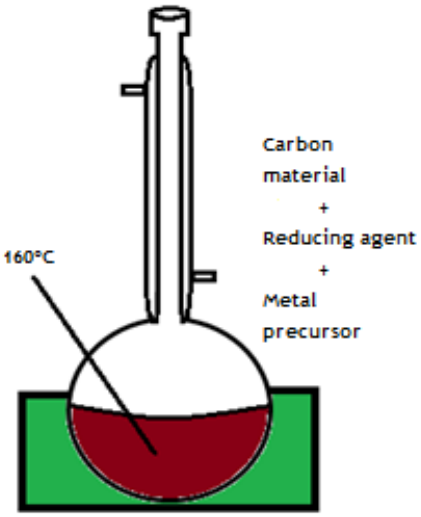


***Figure 6** – Simple schematic of Platinum deposition in a two-round bottom flask*

Graphene as electrocatalyst support

Graphene consists in a single-atom-thick sheet with a hexagonal shape arrayed in sp2-bonded carbon atoms. It presents a 2D form and it is characterized by a high specific surface area (theoretical 2600 m^2/g). Its properties can be "apparently" changed to an almost 3D form, resembling graphite by an oversimplification of aggregated sheets [11].

From an economically point, dispersions of graphene can present a good solution as a source of an ultrahigh surface area substrate. Adhering metal particles to 2D graphene sheets will allow inhibiting the aggregation of graphene sheets, guaranteeing a very high surface area [12].

In order to obtain electrocatalyst supported in graphene, using graphite, an intermediate graphene oxide must be obtained. Reduced graphene oxide is prepared from graphite nanoparticles. The graphite oxide (GO) is obtained by oxidation of graphite in the presence of an oxidant, such as a mixture of sulphuric acid (H_2SO_4) and potassium permanganate ($KMnO_4$) [26]; the GO is then exfoliated, originating graphene oxide. Oxygen functional groups are present in the surface of graphene oxide platelets and can be used as anchoring sites for platinum precursor salts [10]. However, graphene oxide is an electrical insulator, so the reduction of the GO must be achieved in order to recover the honeycomb formation [27]. So, graphene oxide is chemically reduced to reduced graphene oxide, which has higher electrical conductivity than graphene oxide.

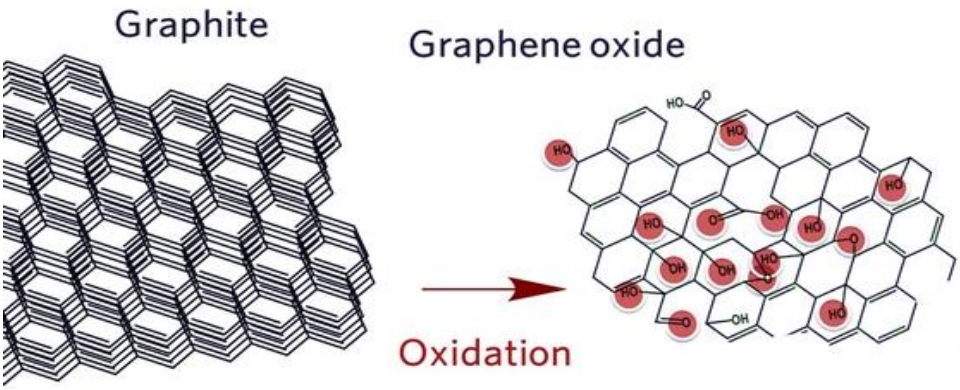


***Figure 7** – Molecular changes between Graphite and Graphene Oxide, considering the formation of surface groups Adapted from [27].*

To produce graphene oxide many procedures have been used using graphite and graphene. In 1958 Hummer developed a method used most commonly today [28]. This process uses $KMnO_4$ as graphite's oxidant. In 2010, Tour et al. developed a protocol that generates a reduced quantity of toxic gases with an increasing efficiency [26].

2.5 Characterization Techniques

Thermogravimetric Analysis

TGA consists in a technique of measuring the percentage weight loss of a test sample while the sample is heated at a uniform rate in a specific environment. The weight loss over a precise range of temperature provides an indication of the composition of the sample, including volatiles and overall thermal stability [29]. This analysis allows quantifying loss of solvents and water, verifying a possible decarboxylation, oxidation, amount of metallic catalytic remaining after the test is concluded, etc. In a practical approach, a TGA has a precise balance and a furnace, in which the sample is heated or cooled and the temperature and mass recorded. A gas purge controls the atmosphere, being this gas inert or reactive, flowing over the sample [30]. Figure 8 represents an example of a TGA curve in which the degradation of the material occurs at, approximately, 400ºC [31].

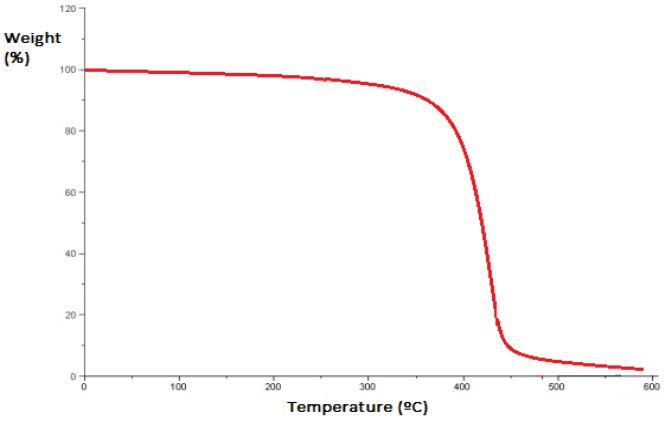


Figure 8 – Example of a TGA curve.

Cyclic voltammetry

CV consists in a potentiodynamic electrochemical measurement and it is commonly used to study fuel cell electrodes, regarding redox potentials. CV, in fuel cells and specifically in fuel cell electrodes, can determine catalyst activity by sweeping back and forth between two voltage limits while the current response is registered [13, 32].

In the cyclic voltammetry testing of fuel cell electrodes developed in this project it is used a conventional three-electrode system. In Figure 9 is present a scheme of this assemble [32]. A Pt mesh with a surface area considerably larger than the working electrode is commonly used in this system as a counter electrode (CE). The purpose of a counter electrode with bigger proportions is to assure the electrochemical reaction happening is fast enough in order to allow the reaction occurring on the working electrode. The reference electrode (RE) must be very close to the working since a higher distance potentiates an IR drop (voltage drop caused by electrolyte conductivity, distance between WE and RE and the current) [33], which may affect the quality of the results. The most common RE are $Pt/H_2/H^+$, $Ag/AgCl/Cl^-$, saturated KCl/AgCl and $Hg/HgCl_2/Cl^-$ (calomel) [1]. This test is made with a constant flow rate of an inert gas, most commonly nitrogen.

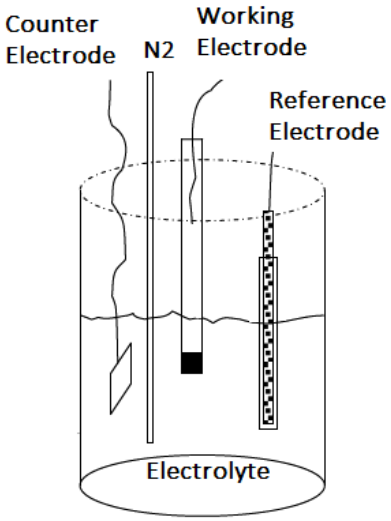


***Figure 9** – Configuration of the 3 electrode system with N_2 flow. Adapted from [1]*

Results of a CV test are commonly presented as current density vs. potential of the working electrode and it exhibits various peaks correspondent to the oxidation and reduction reactions. Figure 10 presents a typical voltammogram [34] in which Q' and Q'' represent the charge exchange during the electro-adsorption and desorption of hydrogen on Pt sites. The filled area is the contribution of the double layer charge.

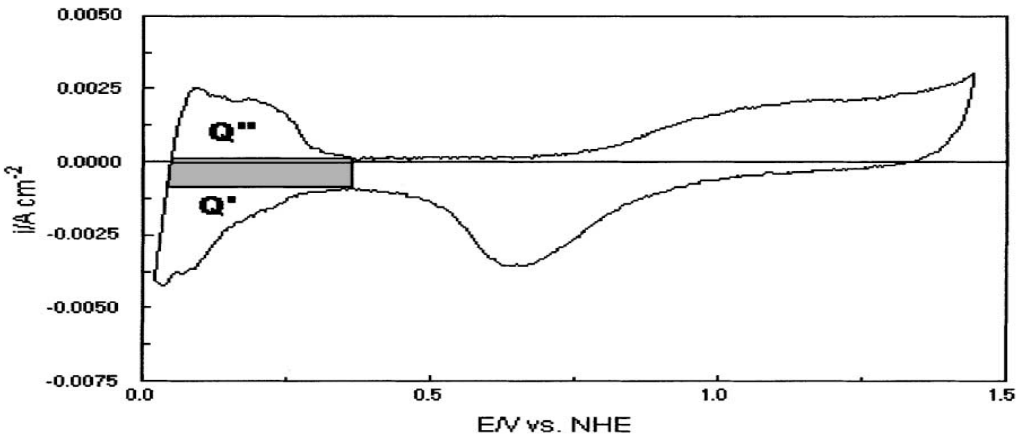


***Figure 10** – Cyclic voltammogram on Pt/C in the potential range 0 – 1.4 V [34].*

Figure 11 presents a cyclic voltammogram of a commercial carbon support with platinum as WE in 0.5 M of sulphuric acid, with saturated KCl/AgCl as RE.

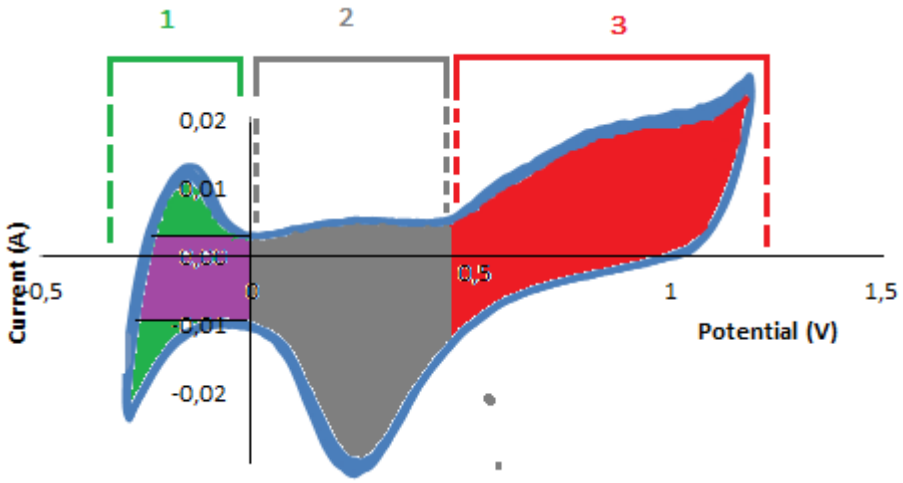


***Figure 11** - Different phases in a CV performed with a 3 electrode system, in sulphuric acid 0.5M with a slew rate of 50 mV/s. The electrode used was Sigracet 10CC (0.5 mg Pt/cm^2).*

Region 1 corresponds to the desorption process of adsorbed hydrogen from the surface of the Pt catalyst. The second highlighted region (region 2) represents the double layer charging and discharging. The region 3 presents two peaks, which corresponds to the formation of OH and O, respectively, on the surface of Pt catalyst. Following, Pt starts to oxidize and forms an oxide layer. After this last peak, the oxygen gas evolution is the most preponderant phenomenon, resulting in a reverse scan. Compared to the peak of oxide formation, the peak of the oxide reduction occurs at lower potentials. Throughout the cathodic scan, the underpotential deposition of hydrogen atoms is verified from the reduction of the protons. At last, the peak related to the adsorption reaction is similar to the one verified in the desorption phase [35, 36]. The integration of the hydrogen desorption/adsorption peaks allows estimating the electrochemical surface area (ECSA) of the electrocatalyst. The shaded area in Figure 10 consists in the charge density arising from the hydrogen adsorption on the Pt catalyst during the reverse sweep of the CV [37]. The ECSA of an electrocatalyst gives important knowledge regarding the number of electrochemically active sites per gram of catalyst [38]. Some of the most usual reactions used to characterize electrodes are the hydrogen adsorption/desorption (HAD).

$$Pt - H_{ads} \Leftrightarrow Pt + H^+ + e^- \quad \textbf{(1.1)}$$

The ECSA of the catalyst is calculated from the charge density (q_{Pt}) obtained from the CV, the charged needed to reduce a monolayer of protons on Pt (Γ=210 μC/cm$^2_{Pt}$) and the Pt loading in the electrode (L).

$$ECSA(cm^2_{Pt} \,/\, g_{Pt}) = \frac{q_{Pt}}{\Gamma \cdot L} \quad \textbf{(1.2)}$$

Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a commonly used analysis which evaluates electrochemical systems and measures the frequency dependence of the impedance (Z). It is a commonly used technique to characterize fuel cells. To achieve this, a perturbation, like a small potential or current, is imposed and the response is registered. The result given by the system is a sinusoidal current density with the same frequency and phase shifted.

The linearity of the system is important to implement an EIS, therefore, the perturbation used in the impedance measurements must have a small voltage signal. This value is usually 5 mV or 10 mV, providing a pseudo-linear response [13, 17, 39, 40]. The perturbation is usually applied over a wide range of frequencies. This methodology allows understanding the importance and influence of each process in a fuel cell, like mass transport in the gas diffusion electrodes, charge transport in the PEM, electrochemical reaction kinetics and ohmic resistance [17, 41-43].

The catalyst and its loading, the electrolyte content in the catalyst layer, the PTFE content, the membrane, the GDL and its porosity, as well as the operation conditions, affect the outcome of this technique, when applied to a PEMFC [44].

The parameters that define the impedance are the real impedance (Z'), the imaginary impedance (Z''), the impedance magnitude (|Z|) and the phase angle (θ). Considering the great amount of information provided by this technique, graphical representation typically consists in a plot of the complex impedance versus real impedance (Z' and Z'') as well as plots with the magnitude of the impedance and phase as a function of frequency. The former is named a Nyquist plot while the latter is a Bode plot [17, 41, 44]. In a typical fuel cell Nyquist plot, and considering a simple example, two pronounced arcs can be distinguished, Figure 12 a) [13]. These account for the charge transfer resistance at high frequencies and intermediate frequencies. A third semi-circle could appear, representing mass transfer processes at low frequencies. The ohmic loss (obtained when the Nyquist plot crosses the real axis) may be understood as the sum of the several contributions, like contact resistances and ohmic resistances of cell components (the membrane, GDL, catalyst layer, etc.). The size of each semi-circular peak in a Nyquist plot reflects the respective magnitude of the activation loss of the component (cathode or anode) [13]. Using a H_2/Air as feeding gases, the charge transfer resistance of both anode and cathode are condensed in one semicircle, which is attributed mostly to the cathode impedance, Figure 12 b) [13]. This is due to the fast hydrogen oxidation reaction and mass transport [39, 44, 45]. It is clear that the losses related with the cathode are the most preponderant in the entire cell [13].

Figure 12 shows examples of Nyquist plots.

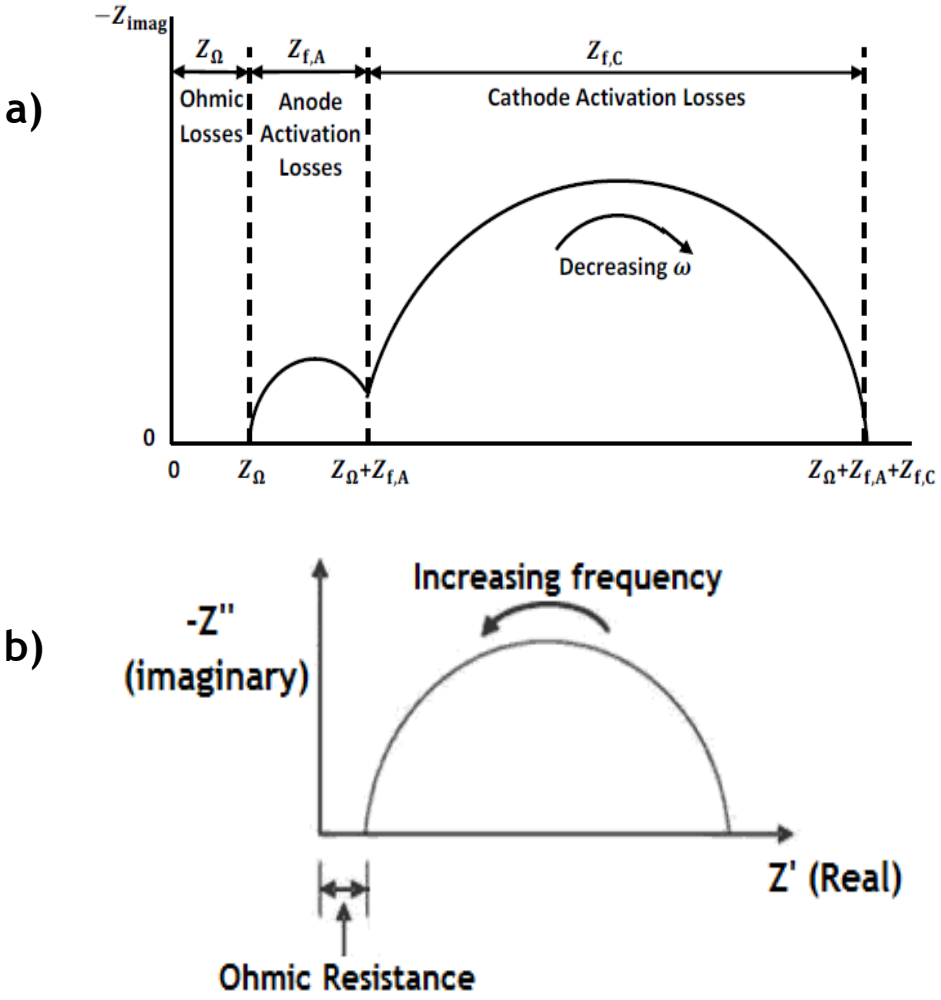


***Figure 12** – Examples of Nyquist plots for a simple fuel cell impedance model a) considering the losses registered in a double loop plot and b) with a single loop plot [13].*

3 TECHNICAL DESCRIPTION AND PROCEDURES

The goal of this work is to evaluate graphene as a potential electrocatalyst carbon support of HT-PEMFC. This involves several working steps:

i. Graphite/Graphene oxidation into graphene oxide;
ii. Platinum deposition in several supports and production of electrodes;
iii. Characterization of the materials and electrodes (TGA, TEM, ICP and Cyclic Voltammetry);
iv. Production of a MEA;
v. Characterization of the MEA in a fuel cell arrangement (EIS).

3.1 PRODUCTION OF GRAPHENE OXIDE

In this work two different methods were used to oxidize commercial graphite and graphene, the modified Hummers' method and the Tours' method.

In modified Hummers' method, carbon material was added to concentrated H_2SO_4 (sulphuric acid) and cooled to 0ºC. Then $KMnO_4$ (potassium permanganate) was added. The solution was stirred at 35ºC for 2 hours. At 0ºC, water was added (using an ice bath) and finally H_2O_2 (30% VWR) is added until no gas was produced. The solution was decanted and the solids carefully washed with water and centrifuged. The graphene oxide was dried at 80 °C for 24h [26, 46]. In the Hummers' method only graphite (American Elements, APS: 7-11 μm) was oxidized. To obtain different oxidation degrees, diverse mass ratios between graphite and $KMnO_4$ were used (wherein referred as, 1:1, 1:3, 1:6). Graphite that was treated with a similar process to oxidation, without the addition of $KMnO_4$, was used as reference (1:0).

Tours' method was firstly presented in "Improved Synthesis of Graphene Oxide" in July 2010, being one of the most downloaded scientific papers in that month [47]. An acid solution of H_2SO_4/H_3PO_4 with 9:1 ratio was made. This acidic solution was added to recipient with the carbon support and $KMnO_4$. The mixture was left in agitation at 500 rpm and 50ºC overnight. The solution was cooled to room temperature and then 200 mg of deionized water (ice) was added to the solution as well as of H_2O_2. Figure 13 shows the oxidation in development and the final result of GO from graphite, using Tours' method.

***Figure 13** – Evolution of the mixture containing the oxidation of the GO from graphite with a degree of oxidation of 1:3, using Tours' method.*

The mixture was then centrifuged in an eppendorf Centrifuge 5810 R. Several centrifugations were made: without previous wash, washed with 100 mL of deionized water, washed with 100 mL of HCl (32%) and washed with ethanol (2x). Every centrifugation performed was at 4000 RPM for 30 minutes each and an average of 2 centrifugations per washing phase. Few times more spins were performed, since the phase separation was not ideal after just two spins.

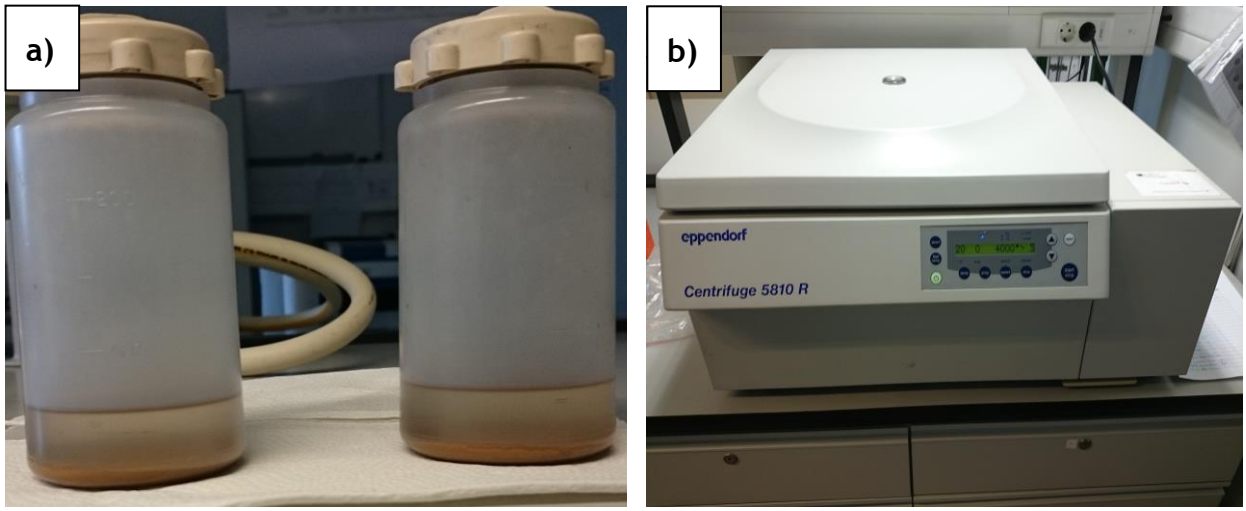


***Figure 14** – a) Example of a stage of purification after a centrifugation of 30 min with 4000 RPM and b) centrifugator used.*

After centrifugations, the sample was mixed with 100 mL of ether and then filtered with NL17-Membrane Filters Polyamide 0.45 µm with 50 mm of diameter, under vacuum. The solid was removed and left drying in vacuum overnight at approximately 30º C. In the next image it

is presented the result of the filtration of the GO from graphite with a degree of oxidation of 1:3. Completed this step, the samples were left lyophilizing for two days.

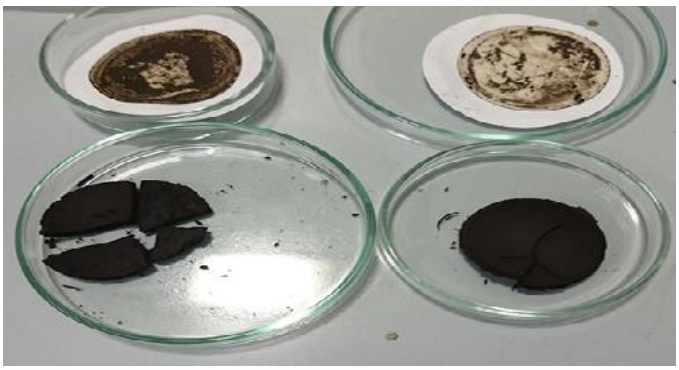


***Figure 15** – Results of the filtration of the mixture with reduced GO (1:3) with platinum.*

In this method also graphite from American Elements was used, in order to obtain different degrees of oxidation (1:3) and (1:6), and graphene from XG Sciences (xGnP-M-5 and xGnP-H-5). The two samples of graphene differ on the thickness and surface area, maintaining density and electric conductivity. The number 5 present in both names refers to the diameter of the average particle (5 μm). The graphene H5 possesses particles with an average thickness of, approximately, 15 nm and a surface area of nearly 50 to 80 m^2/g. On the other hand, the graphene M5 has particles with 6 to 8 nm of typical thickness and 120 to 150 m^2/g as usual surface area [48, 49]

In Table 1 all the oxidations performed with both methods are showed.

***Table 1** – Oxidations developed with Tour and Hummers' methods.*

	Carbon source	**Carbon:$KMnO_4$**
Hummers' Method	Graphite	1:0
		1:1
		1:3
Tours' Method	Graphite	1:3
		1:6
	Graphene M5	1:3
		1: 6
	Graphene H5	1: 3

3.2 Platinum Deposition

Typical reducing method used previously in LEPABE [9, 50] was used to produce reduced graphene oxide supported electrocatalyst. GO (with different oxidation degrees) is dissolved in an ethylene glycol (EG) solution (95:5) and the required amount of a platinum precursor ($H_2PtCl_6 \cdot 6H_2O$, Sigma-Aldrich) in EG is added drop wise, with agitation at room temperature. NaOH is added to adjust pH above 13 and the mixture was heated to 160 °C (achieved roughly 25 minutes after) and refluxed for 3 h, Figure 16 a). For comparison with carbon black VULCAN XC72R GP-3909 (CABOT) and commercial graphene were also used.

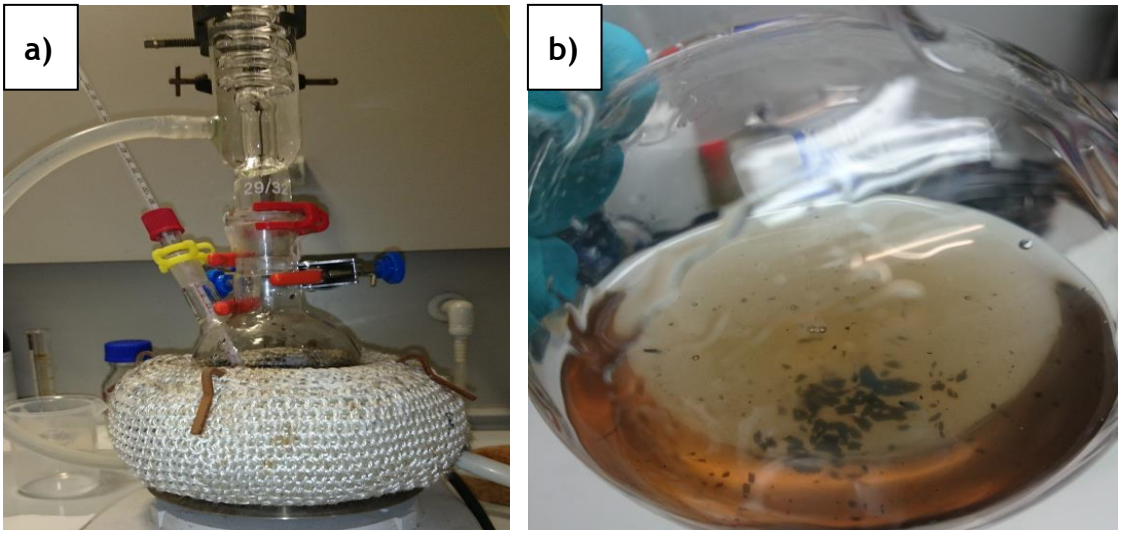


***Figure 16** – a) Structure of the platinum chemical deposition and b) GO sedimentated in the final solution.*

After this, the mixture in the flask rested overnight. In the next day, the material was filtrated with a Büchner funnel and a filter paper (Whatman) with 2.7 µm pore size. After filtration, the solid was repeatedly washed with distilled water. The remaining material was dried overnight at 70ºC and, in the following day, the solid was weighted and carefully stored. This procedure was performed 11 times.

3.3 Production of Electrodes

A homogeneous suspension of the catalyst powder (synthesized in the previous section) was prepared with isopropyl alcohol. Catalytic active layers based on carbon supports are spray-dried on a commercial Sigracet GDL microporous surface (SGL Carbon) followed by drying at room temperature overnight. The catalyst load was obtained based on the difference

between the weights of microporous GDL before and after the spray-drying. Figure 17 shows electrodes prepared.

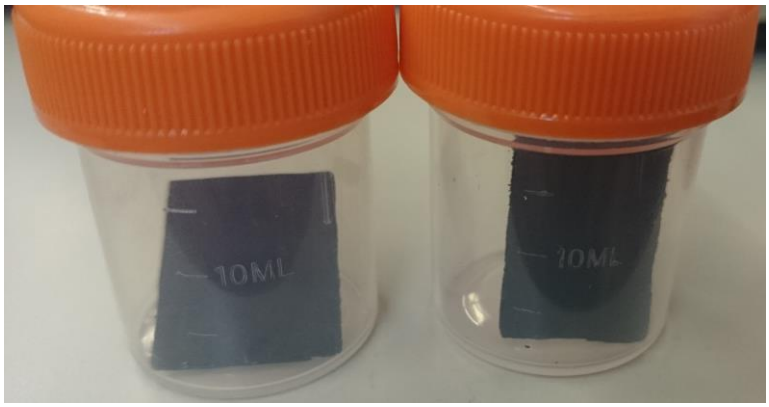


Figure 17 *- Electrodes prepared with GO from graphite 1:3 developed according with Tours' method.*

3.4 CHARACTERIZATION OF THE MATERIALS AND ELECTRODES

Characterization of prepared materials

All the oxidized as well as the reference materials were analyzed by thermogravimetric analysis (TGA). To evaluate the metal content of the electrocatalyst powders both TGA and, for some of the samples (the materials prepared with Hummers' method), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) were performed. Furthermore, the microstructure and morphology of a part of the samples (the materials prepared with Hummers' method) were characterized by field emission scanning electron microscopy (FE-SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector.

TGA was performed in a NETZSCH TG 209 F1 (Figure 18). The testing powders were heated from 30ºC to 850ºC with O_2 and (20%) and N_2 (80%). As a safety measure, a protective purge with Nitrogen was activated. Both purges had a flow rate of 30 mL/min. To avoid the rapid combustion (explosion) of the samples, a small heating rate was defined (3K/min) and the mass of the material was always kept below 4 mg. The graphene oxide samples prepared by the Hummers' method were tested in the same equipment, in O_2 until 950ºC with a heating rate of 3K/min.

***Figure 18** – TGA equipment used and computer with correspondent software.*

Given that the NETZSCH TG 209 F1 was not completely available during the entire project, due to malfunction of the thermocouple, another equipment (with similar characteristics) was used. Due to time constrains, only a part of the samples were tested in both equipment.

For ICP-AES analysis 30 mg of powder was used to prepare 1mL aqueous solution and the analysis was carried out in Horiba Jobin-Yvon, model Ultima, equipped with a RF 40.68 MHz generator. The sample analyzed by ICP-AES was GO 1:3 prepared with the modified Hummers' method.

The samples analyzed by TEM, GO 1:0, 1:1 and 1:3 prepared by Hummers' method were prepared by dropping a microliter amount of powders suspension in ethanol, previously sonicated, into a conductive layer of amorphous carbon.

Characterization of electrodes

The produced electrodes were characterized by cyclic voltammetry, using a 3 electrode configuration and by EIS using a typical PEMFC configuration, after assembling a high temperature MEA. The electrochemical characterization was performed by a Zahner electrochemical station, Figure 20, using Thales software, Figure 21 (module for CV shown).

In order to obtain the ideal conditions for testing the produced samples by cyclic voltammetry, several parameters were optimized like slew rate, the position of electrodes, concentration of H_2SO_4, potential and current limits and nitrogen purge flow rate. This study was performed using a commercially available electrode 10597 GDE S10 CC Sigracet 10 CC with 0.5 mg Pt/cm^2. Figure 19 shows the evolution of the assembled system. The final assembly system allowed to stabilized the electrodes and use a lower acid volume.

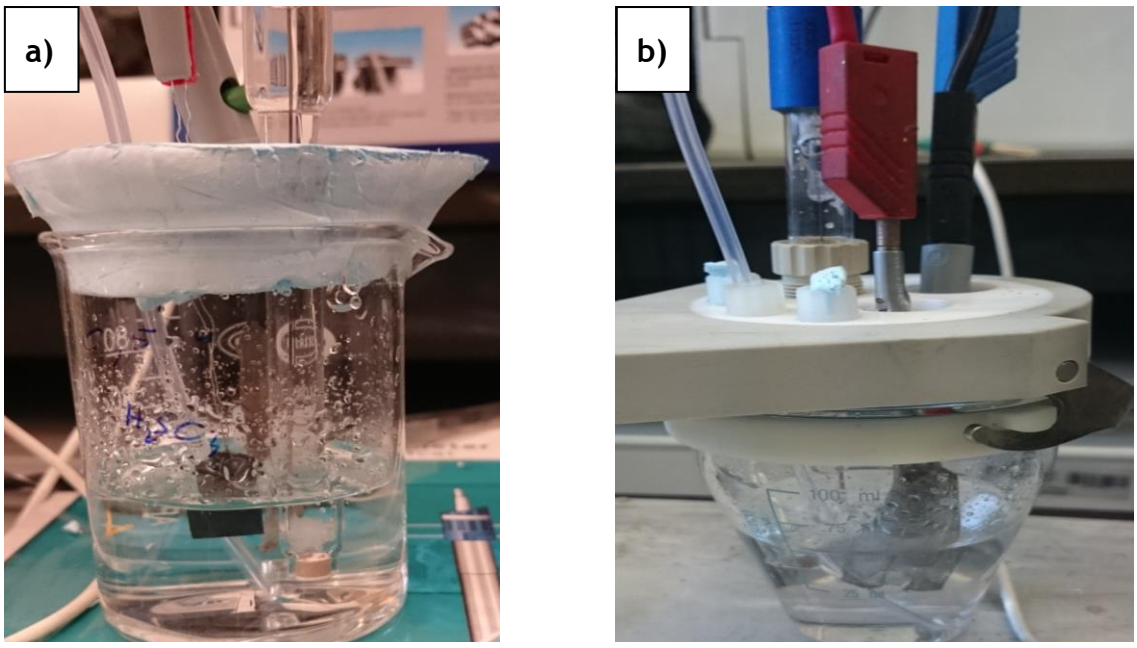


***Figure 19** – Evolution of the schematic of the 3 electrode system used to develop cyclic voltammetry. a) and b) are presented chronologically.*

The electrodes were kept close in order to reduce the ohmic drop [33]. The acid concentration that provided the best results was 0.5 M, which is consistent with many scientific literature [36, 38, 51]. The slew rate of 50 mV/s is congruent with many works developed before [1, 9, 52, 53]. The voltage range used in the cyclic voltammogram performed to the samples was between 0V and 1V.

***Figure 20** – Zahner electrochemical station IM6ex.*

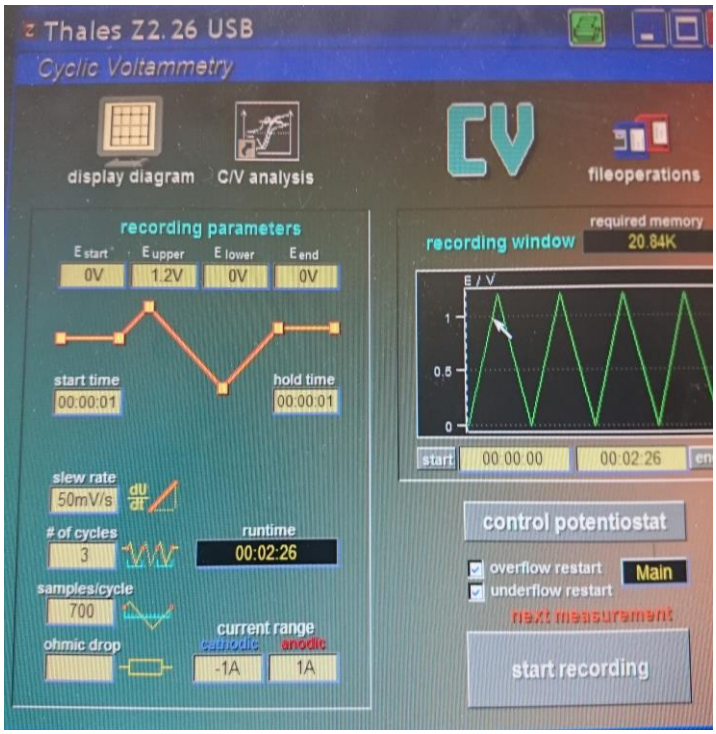


***Figure 21** – Cyclic voltammetry module from Thales software.*

One of the produced electrodes (GO 1:3 prepared with Hummers' method) was assembled with a TPS membrane as polymer (Advent) previously soaked in phosphoric acid for 48 hours, Figure 22. The graphene based electrode was used at the anode side while at the cathode side a commercially available electrode was used (10597 GDE S10 CC Sigracet 10 CC with 0.5 mg Pt/cm^2). The electrodes used had an area of 5 cm^2. The MEA was placed in an Electrochem cell, Figure 23, and tested in an in-house built fuel cell test station. The system was controlled using an application developed in LabView (National Instruments). The MEA prepared was tested at atmospheric pressure at 160 ºC, with a hydrogen flow of 0.100 L·min^{-1} and air flow of 0.300 L·min^{-1}. Activation of the MEA was performed potentiostatically at 500 mV. With voltages of 400 mV, several EIS were performed to evaluate the progress of performance. EIS was obtained in the frequency range from 30 kHz to 100 mHz with perturbation amplitude of 5 mV.

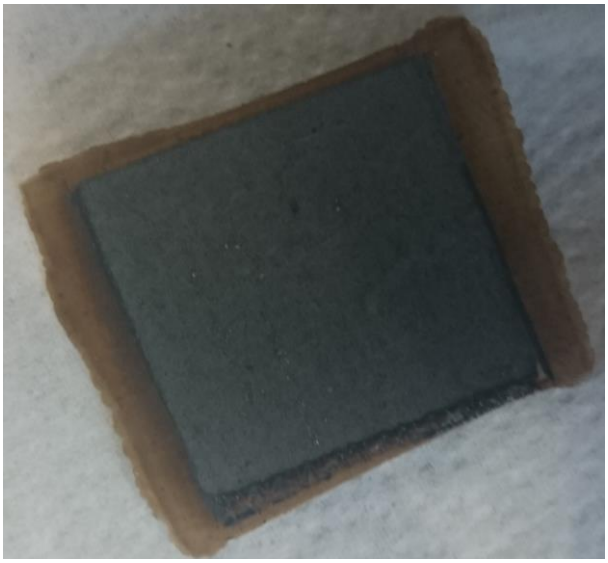


***Figure 22** – MEA assembled with a commercial sample with 0.5 mg Pt/cm2 and a homemade one as electrodes. Between them is a polymer soaked in phosphoric acid for 48 hours. The electrodes have an area of 5 cm^2.*

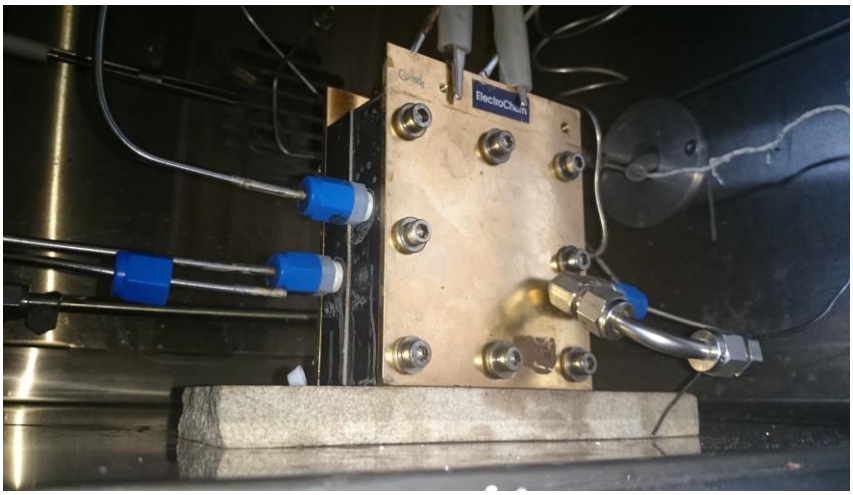


***Figure 23** – Electrochem single cell assembled.*

4 RESULTS AND DISCUSSION

4.1 THERMOGRAVIMETRIC ANALYSIS

Graphene oxide characterization

The influence of synthesis conditions on the properties of graphene oxide was evaluated by TGA. Figure 24 shows the weight loss as a function of the temperature in the presence of oxygen for the oxidized samples with Hummers' Method (1:1, 1:3) and the 1:0 reference.

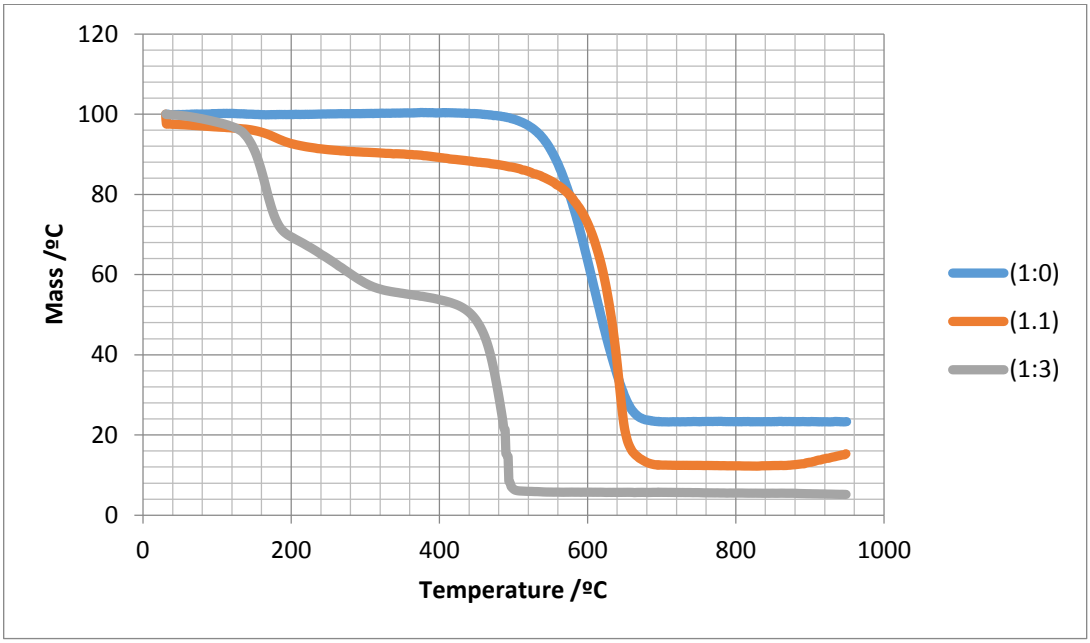


Figure 24 *- Weight loss as a function of the temperature, in the presence of oxygen, for the graphene oxide samples, with different oxidation levels (1:1 and 1:3), obtained with Hummers' method, and reference 1:0.*

Lower ratios between graphite and $KMnO_4$ lead to higher weight losses between 200 - 400°C, Figure 24, indicating the presence of higher amount of oxygen surface groups. The introduction of oxygenated groups, by using the Hummers' method, leads to thermal instability. So, the lower the ratio between graphite and potassium permanganate is (1:3>1:1>1:0), the lower is the decomposition temperature of graphene oxide.

The curves obtained from the TGA performed with oxidized material using Tours' method are shown in Figure 25, for graphite and graphene M5.

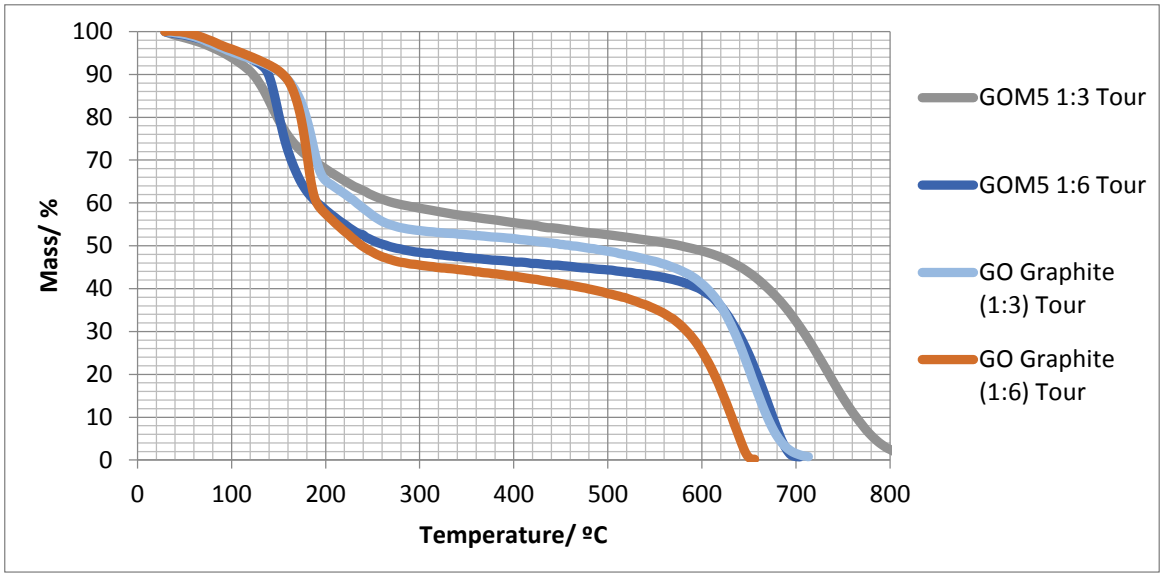


Figure 25 *- Weight loss as a function of the temperature, in the presence of oxygen atmosphere, for the graphene oxide samples, with different oxidation levels (1:3, 1:6), obtained with Tours method, for graphite and graphene M5.*

The results obtained with the Tours' method indicate a similar behavior as the ones obtained with the Hummers' method. Lower ratios between graphite or graphene and $KMnO_4$ lead to higher weight losses between 120ºC and 220ºC, showing a relation between an increase of the amount of $KMnO_4$ and the increase the quantity of functional groups at the surface, Figure 25. This increase leads to a lower decomposition temperature of the materials in study.

Carbon Black is the most used carbon support [9], and therefore a platinum deposition using EG and $H_2PtCl_6 \cdot 6H_2O$ was performed for comparison, Figure 26.

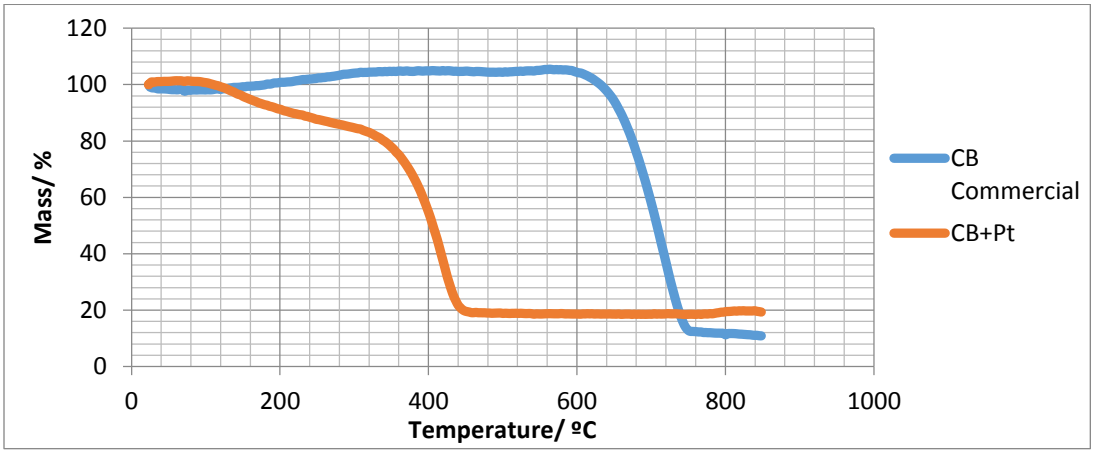


Figure 26 *- Weight loss as a function of the temperature for the platinum supported in carbon black and carbon black. EG was used as a reducing agent and H2PtCl$_6$·6H2O 2 as a platinum precursor.*

Considering that the platinum deposition on the carbon surface is targeting 20% of the total mass, the residual mass obtained with this material is within expected, Figure 26. However, the mass variation between 120ºC and 300ºC in carbon black with platinum was not anticipated. Since the ebullition temperature of the EG is approximately 200ºC, it can be assume that a small amount is still in the powder. The commercial sample, without platinum, suffers slight mass changes due to sporadically instability of the TGA equipment.

Figure 27 shows the weight loss as a function of the temperature in the presence of oxygen for the platinum depositions in the supports produced from Hummers' Method, using $H_2PtCl_6 \cdot 6H_2O$ as a platinum precursor. The residual mass obtained was attributed to platinum. Commercial carbon black supporting platinum (labeled 20% platinum) was included for comparison.

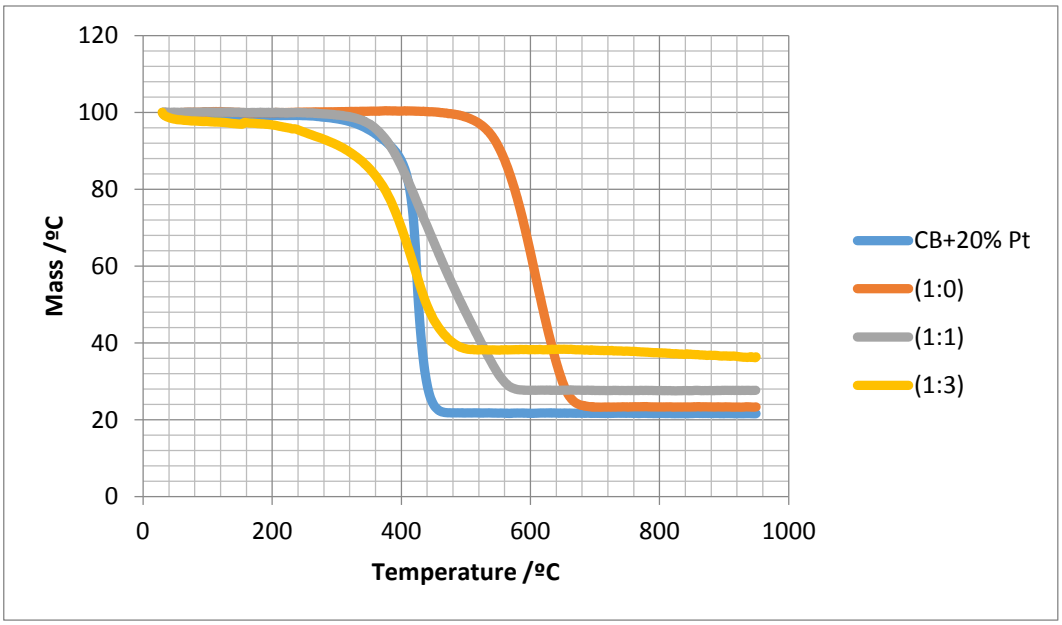
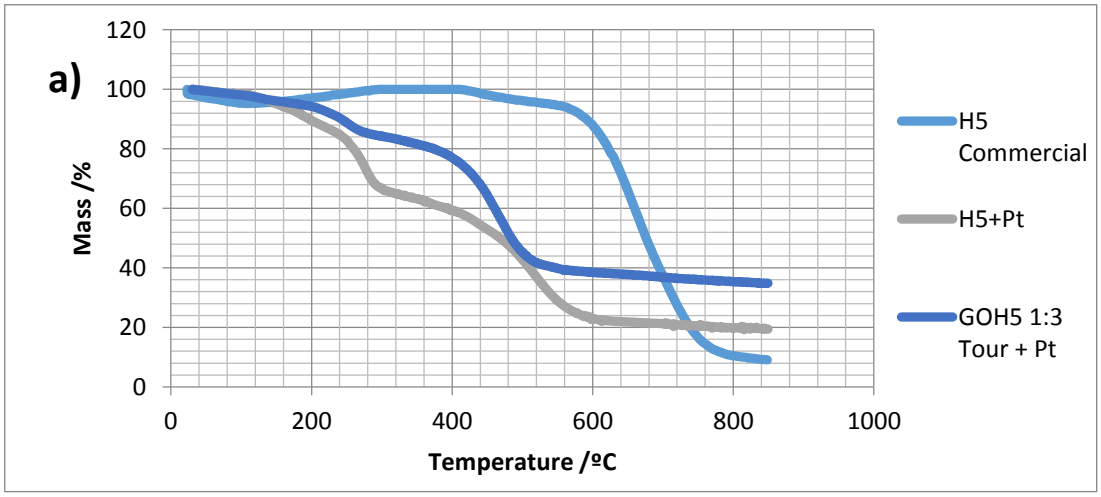
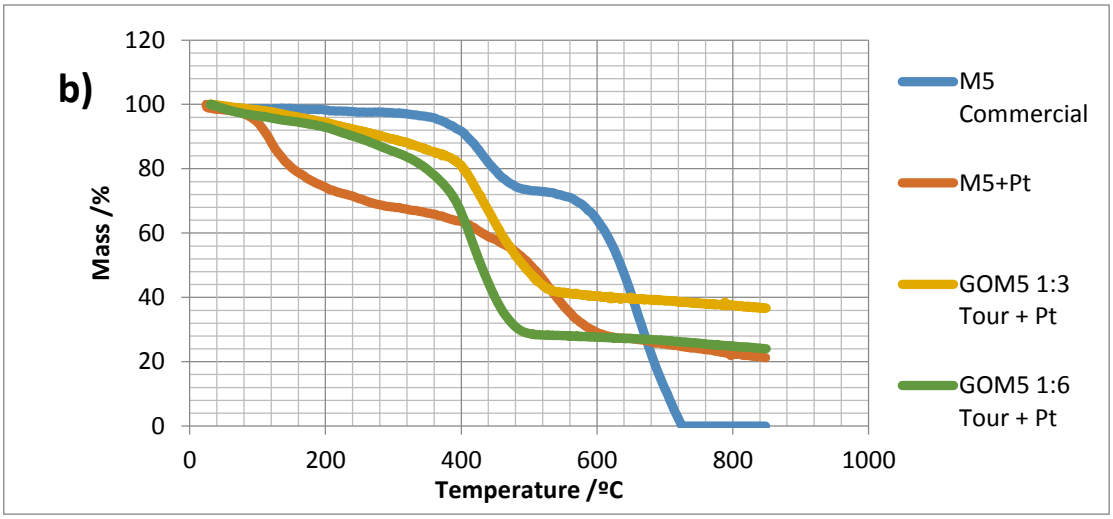


***Figure 27** - Weight loss as a function of the temperature for the platinum supported in reduced graphene oxide (1:1 and 1:3) and reference 1:0. EG was used as a reducing agent and $H_2PtCl_6 \cdot 6H_2O$ as a platinum precursor*

For the analyzed samples, the degradation temperature ranges from 300°C to 700°C, being higher for platinum supported on graphene oxide that had lower oxidation degree. For the samples 1:1 and 1:3, a higher amount of platinum than expected (20%) was obtained, showing a possible carbon loss during the deposition process. Also, it is observed higher degradation temperature and a higher amount of platinum with the increase on the oxidation degree (1:3>1:1>1:0). Concerning the samples obtained with Tours method, Figure 28 shows the TGA curves of Graphene H5, M5 and graphite based materials, respectively. The curve for the commercially available material, without platinum deposition, was added for comparison.





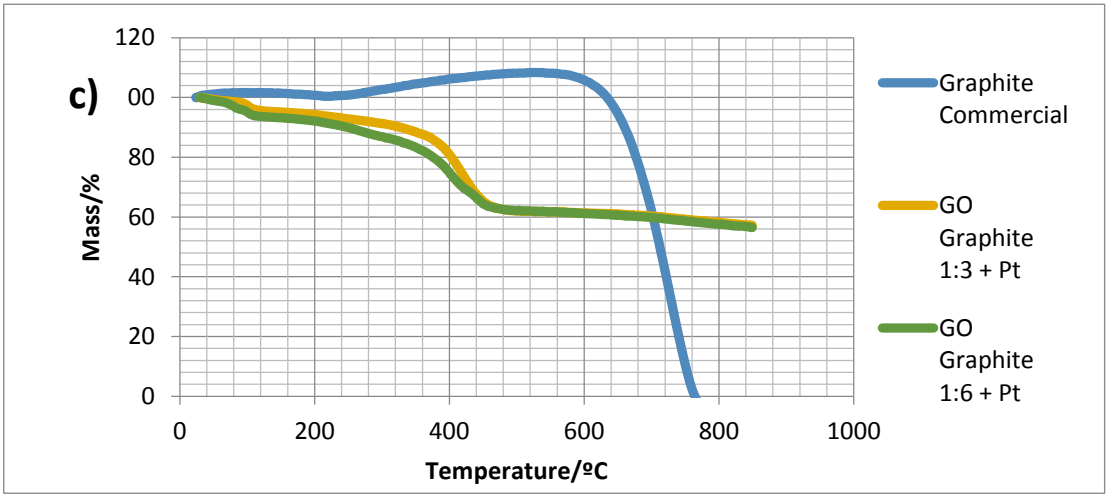


Figure 28 *- Weight loss as a function of the temperature for (a) the platinum supported in reduced graphene oxide and platinum supported based in H5, (b) the platinum supported in reduced graphene oxide based in M5 (1:3 and 1:6) and platinum supported in M5 and (c) the platinum supported in reduced graphene oxide based in graphite and platinum supported in graphite. EG was used as a reducing agent and* $H_2PtCl_6 \cdot 6H_2O$ *as a platinum precursor.*

All the samples related with Graphene H5, Figure 28 a) present equal response until 160ºC, however, the commercial sample without platinum suffers slight variation, with the carbon burning between 560ºC and 760ºC. The curve of the H5 with platinum indicates two clear mass losses, one between 200ºC and 300ºC and another among 400ºC and 550ºC. The first mass loss may be related with residual ethylene glycol still present in the commercial material that was not removed during the platinum deposition. For the oxidized H5 sample the mass loss between 200 and 300ºC is less pronounced and once again the residual value for platinum is higher than expected.

Considering the Figure 28 b) (Graphene M5), the commercial sample M5 with platinum presents a residual mass close to 20%. Again a significant decrease was observed just after 100 ºC. The samples subjected to previous oxidation only have one major weight loss at, roughly, 400ºC. The final mass percentage of the sample with a degree of oxidation of 1:6 is almost 20% while the one with a degree of 1:3 is, approximately, 36%.

Overall, the weight losses up to, roughly, 100ºC is due to evaporation of water and to 200ºC might be due to EG. Weight losses between 150ºC and 300ºC are justified by the release of CO and CO_2 and decomposition of less stable oxygen groups, like carboxylic and anhydride groups. The weight losses above 300ºC can be attributed to the disappearance of more stable oxygen functionalities, like phenol, quinone and carbonyl groups [26, 54].

Figure 28 c) presents the TGA of GO samples prepared from graphite with the Tours' method. Both samples have a major weight loss at, approximately, 400ºC. Higher losses can be seen for the sample 1:6. The residue is roughly 60% for both samples, indicating a considerable loss of carbon support. These results are not similar to the ones obtained with the modified Hummers' method, Figure 27.

As mentioned in the previous section, during the TG examinations with the oxidized samples (1:3 and 1:6) the equipment used had a serious defect with the thermocouple, which might suggest that the sample was not heated to the desire value and/or the heating degree could not be being followed.

4.2 ICP-AES

ICP-AES was used to confirm the results obtained by TGA regarding the platinum content. Table 2 shows platinum amount on the supports (obtained with Hummers' method) according to TGA (residue at 950 °C) and ICP-AES.

For the analyzed samples the TGA are in accordance with the results obtained by ICP-AES.

***Table 2** - Platinum amount (w/w) on the supports according to TGA and ICP-AES techniques. EG was used as a reducing agent and H2PtCl6•6H2O as a platinum precursor.*

Carbon support	Platinum /%	
	TGA	ICP-AES
1:0	23.3	21
GO 1:1	27.7	23
GO 1:3	36.4	37

4.3 TEM-EDS

Electronic microscopy analysis was developed in order to verify the distribution and size of the deposited platinum particles (Figure 29). An analysis on reduced graphene oxide platinum supports (1:1 and 1:3) was made, as well as on platinum supported on reference 1:0. Ethylene glycol was the reducing agent used and $H_2PtCl_6 \cdot 6H_2O$ was the platinum precursor. Commercial platinum supported on carbon black (labeled 20% platinum) was included for comparison. In all TEM images displayed, the grey areas represent the carbon support and the round dark shapes consist in platinum particles. Identification was carried out and confirmed by EDS.

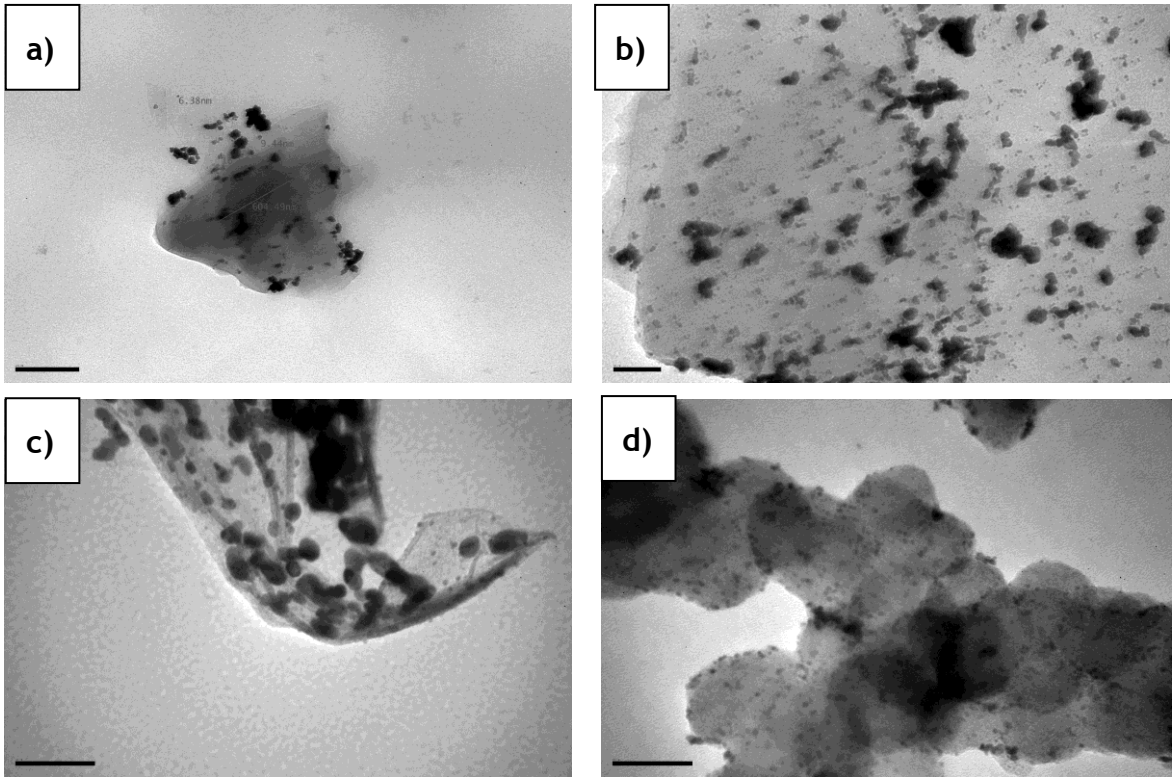


***Figure 29** - TEM images for the platinum supported in reference 1:0 with a magnification of 100000x (a), reduced graphene oxide 1:1 with a magnification of 300000x (b) and 1:3 with a magnification of 500000x (c) and commercial sample of platinum supported in carbon black (labeled 20%) with a magnification of 500000x (d).*

As anticipated, with increasing oxidation of the support, deposition and dispersion rates increase. The reference material, Figure 29 d), shows uniform dispersion and regular platinum particles throughout the support. The samples presented in Figure 29 c) have nearly 10 nm of size, while the ones in Figure 29 d) have between 2 and 3 nm.

4.4 Cyclic Voltammetry

Cyclic Voltammetry allows determining the electrode catalytic activity and estimate the active surface area of the sample in test [13]. The first analyzed samples were commercial Sigracet 10CC - which was used in the optimization conditions - and a catalyst layer produced with JM HISPEC 1000, pure platinum black, applied to gas diffusion layer (Sigracet 35D) with DLR dry spray (1 mg Pt/cm^2) technology.

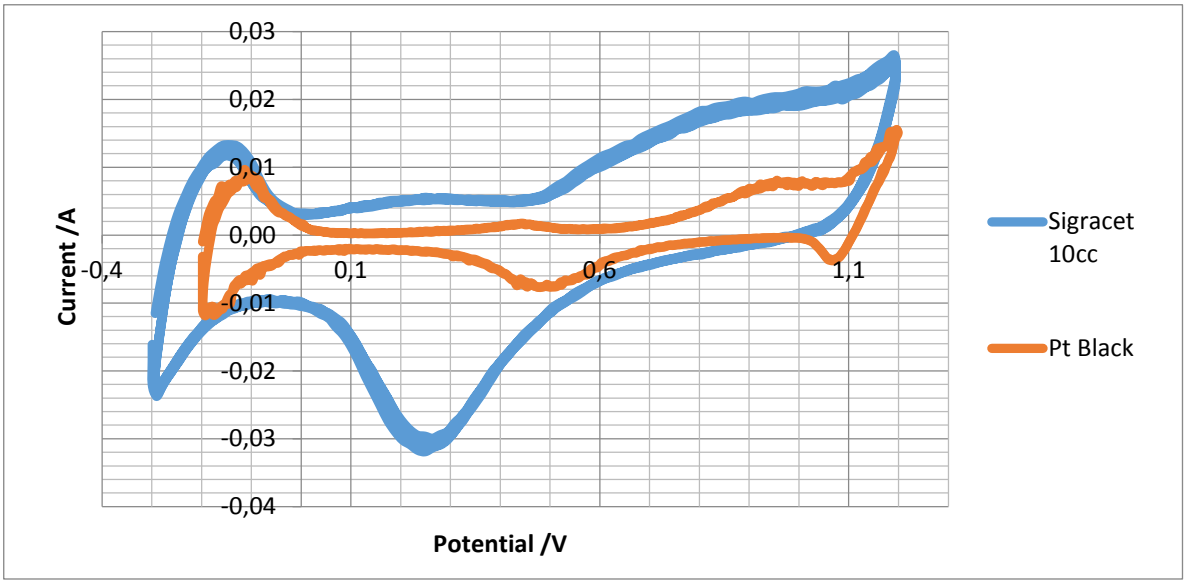


***Figure 30** – Cyclic Voltammograms with two samples. These were obtained with 50 mV/s of slew rate.*

The characteristic peaks related with the formation and reduction of Pt oxide are observed in both curves, between 0.2 V and 1.2 V. The hydrogen adsorption and desorption peaks associated with platinum are in the potential region of -0,2V to 0V [38, 55, 56]. In this range, Sigracet 10CC only presents one peak.

The ECSA was determined in order to compare with available values from similar electrodes in the literature. The integrated area under the adsorption peak represents the total charge related with the H^+ adsorption, therefore, the value of the ECSA can be determined by the Equation (1.2). With the Thales software, a baseline was defined at 2.5 mA and a value of the charge density was determined to be 39.01 mC. So, the electrochemically active surface area of this sample is 37.15 m^2/g Pt. This value is well within the expected considering similar experiments [38, 55].

Following the system optimization the produced electrodes in this project were characterized. Cyclic voltammograms for electrodes produced with platinum supported in graphene oxide (GO obtained with Hummers' Method), are shown in Figure 31.

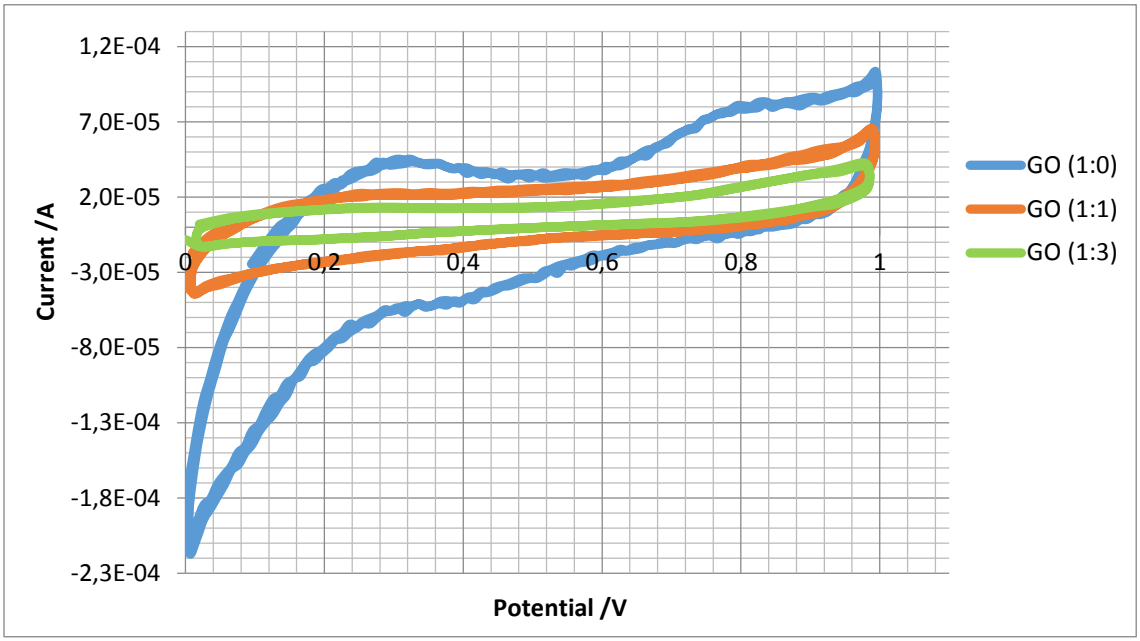


Figure 31 *- Cyclic Voltammograms with three oxidized samples (GO 1:1 and 1:3) prepared with Hummers' method and a reference one (1:0). The electrode area was 1 cm^2. These were obtained with 50 mV/s of slew rate under optimized conditions.*

The GO (1:0) sample has a platinum loading of 0.10 mg Pt/cm^2 , while the GO (1:1) has 0.11 mg Pt/cm^2 and the loading of the GO (1:3) is 0.06 mg Pt/cm^2. For GO (1:0) it was determined the ECSA. A value of 0.134 m^2/g Pt was obtained. This value is very low compared to the one previously obtained for the commercial electrode. The electrodes produced with platinum supported in reduced graphene oxide (1:1 and 1:3) do not present considerable desorption/adsorption peaks, indicating low activity. Should be noted a very low catalyst load [19]. When compared with the referred commercial electrode is discernible that an increase of oxidation of the support used for Pt deposition lead to less perceptible voltammograms. The less oxidized support (1:1) presents a more discernible voltammogram than the more oxidized support (1:3), despite an increased dispersion rates (as observed in Figure 29). The GO 1:3 sample may still present residual oxygenated groups, which could lead to an increased capacitor behavior. However, it is expected that the presence of oxygenated groups affect the current density, promoting more defined curves [57]. The curves obtained are not congruent with this aspect, which could be due to the loading or the platinum dispersion.

An electrode was produced with Pt/GO (obtained by Tours' method with an oxidation degree of 1:3) and characterized. This sample presents a platinum loading of 0.17 mg Pt/cm^2.

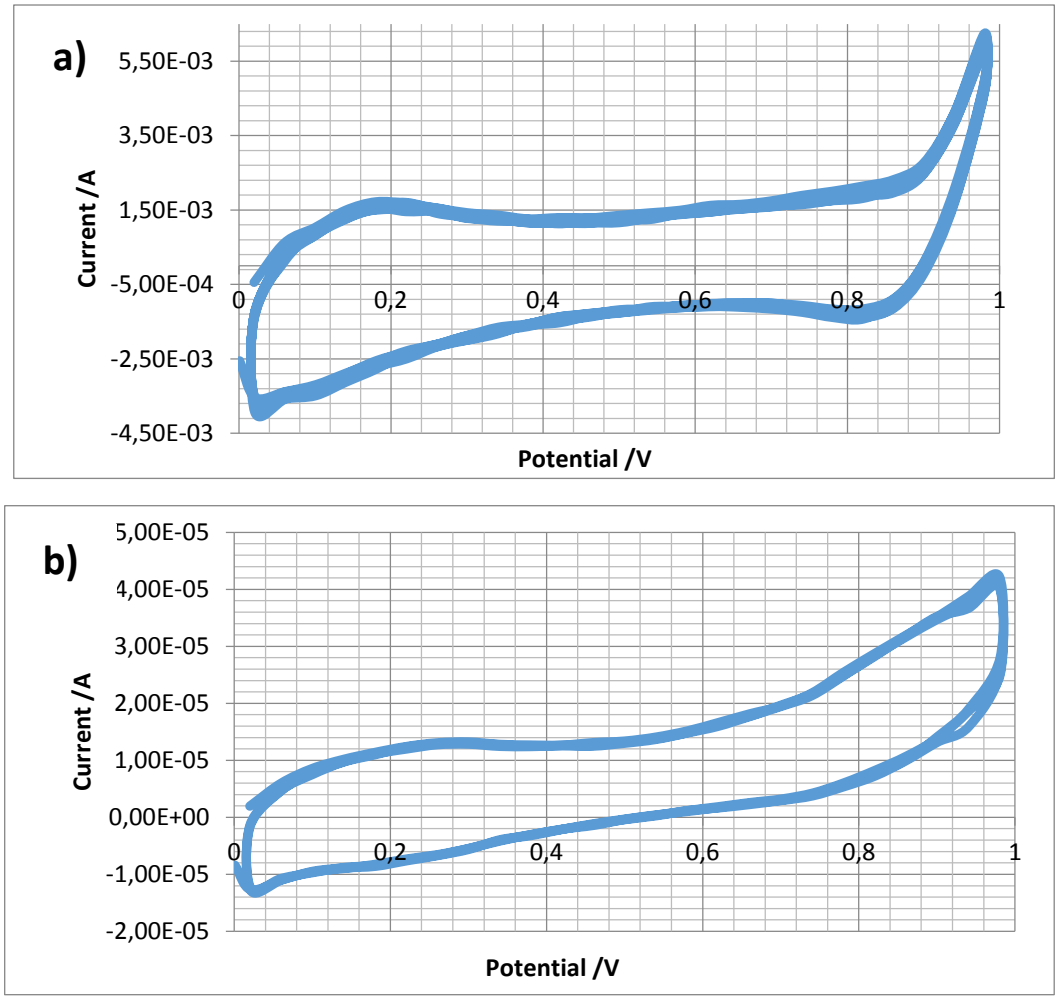


***Figure 32** - Cyclic Voltammograms with a oxidized sample (GO 1:3), prepared with Tours' method (a) and Hummers' method (b). These were obtained with 50 mV/s of slew rate with 1 cm^2 of submerged area.*

The peaks associated with hydrogen adsorption and desorption are more visible in the sample prepared with Tours' method than the one produced by the Hummers', however the latter had a much lower platinum load (0.06 mg Pt/cm^2).

The double layer charging and discharging are clearly seen in the sample prepared with the Tours' method, ranging from 0.35 V to 0.65 V [36]. A clear peak is visible at voltage of 0.2 V. Unfortunately, it is not available the TEM image for this sample.

4.5 HT-PEMFC TESTING AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

A MEA was assembled with the electrode based on Pt/reduced GO 1:3 produced from the Hummers' method, with graphite as carbon source (the one presenting higher dispersion of platinum in the support – Figure 29) and tested at 160ºC. Upon heating an open circuit voltage of 0.904V was obtained. In order to activate the MEA, the cell was kept constant at 0.4V. The evolution of the current obtained is shown in Figure 33.

The obtained values of current are very low (below 12 mA). The membrane was received dry and was doped with phosphoric acid during 48h, at room temperature. It is possible that the amount of phosphoric acid is not enough to provide sufficient proton conductivity. Additionally, the electrodes used did not present a proton conductor on the catalyst layer (and were not optimized), relying in the migration of phosphoric acid from the membrane.

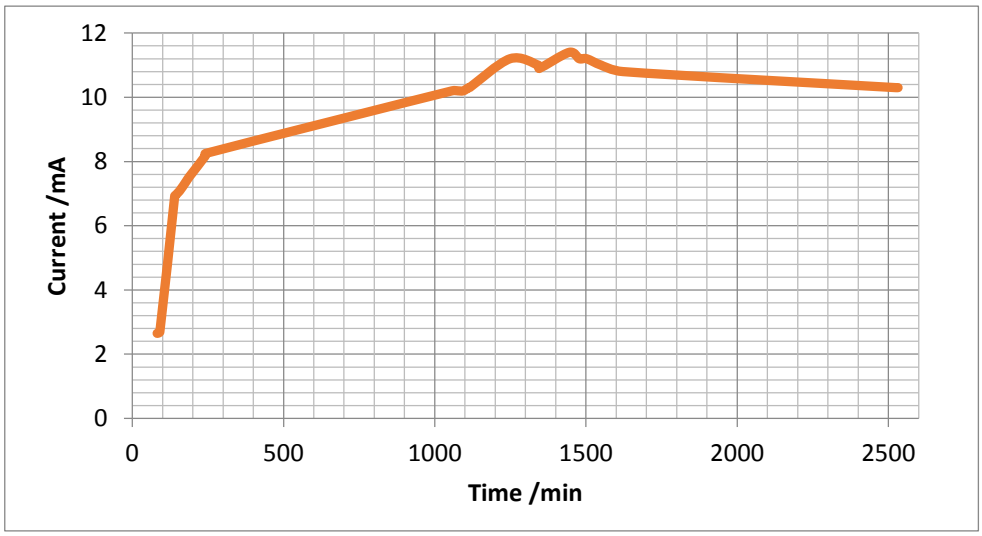


Figure 33 *– Current evolution in function of time in a HT-PEMFC, at 160ºC at atmospheric pressure and with streams of H_2 and Air.*

In attempt to clarify the origin of such low performance, EIS was performed at 3 mA/cm^2, Figure 34.

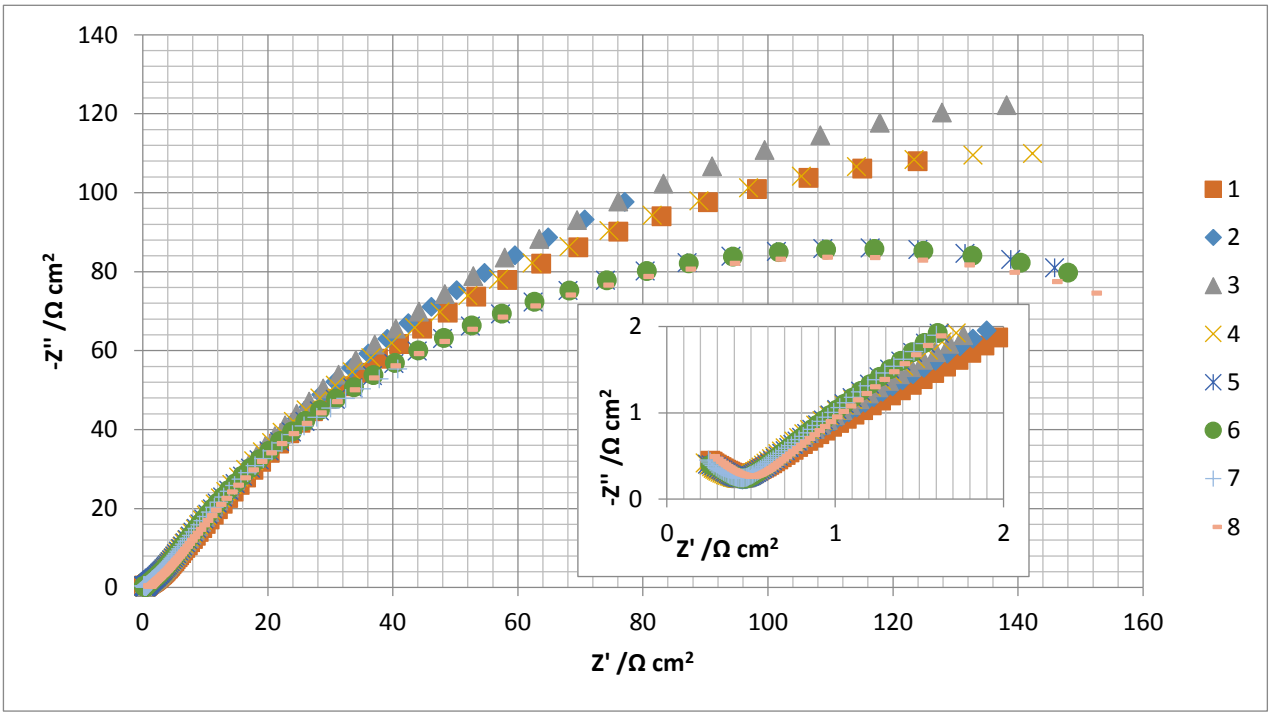


***Figure 34** - Nyquist plot obtained with a HT-PEMFC with a commercial sample (Sigracet 10CC 0.5 mg Pt/cm2) in the cathode and a testing electrode (GO 1:3 Hummers' method) in the anode, at 160ºC. The numbers represent the chronological order in which they have been made (1 the first and 8 the last).*

The interception at high frequencies of an impedance arc with the real axis (R_Ω) represents the total ohmic resistance of the cell [44]. The ohmic resistance was estimated and shows a very high value (c.a. 0.5 Ω/cm^2), considering that the curve does not intercept the axis, therefore it was considered the lowest value verified. The impedance verified is high, indicating that the phosphoric acid amount is extremely low and that there is not enough acid in the interface between the catalyst layer and the membrane to assure the protonic access from the catalyst to the membrane [17, 44].

With increasing operation time there is no change in the ohmic resistance. The loop at high frequencies (not easily visible) related to the anode side suffers soft changes over time and seems to be better defined, probably due to acid migration. For the anode two aspects should be considered: the low values of load (0.22 mg Pt/cm^2) and the presence of the oxygenated species in the catalyst support of the anode. This presence can decrease the electronic conductivity at the catalyst layer.

The more defined semi circle at intermediate frequencies is associated with the cathode side. The cathode impedance is considerably higher than the anode. This masking is not uncommon in fuel cells, since the cathode semicircle overwhelms the anode one [13]. A commercial electrode was used, however, optimized for the use at lower temperatures in LT-

PEMFC and without a suitable electrolyte for high temperature was present. It is possible to understand that the more recent EIS curves show a more defined shape and a semi-circular with a lower diameter, which is attributed to the phosphoric acid migration.

The current density was 3 mA/cm^2, which is a low value [43, 44].

5 CONCLUSIONS

Graphene has raised attention due to its vast range of possible uses. One of the applications considered is the use of this material as platinum support for a PEMFC. The objective of this work is to evaluate graphene as a electrocatalyst support for HT-PEMFC. First, two different oxidation methodologies were used to oxidize graphene and graphite, followed by platinum chemical deposition with $H_2PtCl_6 \cdot 6H_2O$ and using EG as reducing agent. Electrodes were produced with the developed materials and high temperature MEA assembled. TGA and ICP-AES were used to obtain the amount of platinum in each sample, after deposition, the Cyclic Voltammetry was used to obtain the ECSA of the produced electrodes and EIS allowed to characterize the MEA.

The TG analysis indicated that residual oxygenated groups are presented in most samples, even after the reduction process occurred during the platinum deposition. Considering the samples prepared with the Tours' method, GO produced from graphene M5 provides a residual mass closer to the one expected (20%) than the one produced from commercial graphite.

An increased oxidation degree in GO promotes a higher dispersion of platinum and lower particle size, in the samples prepared with GO from Hummers' method. Nonetheless, platinum particles have a higher size than the commercially available platinum supported in carbon black.

A CV setup was developed and optimized using a commercial sample (Sigracet 10CC). The cyclic voltammetry tests indicate that, the lower the oxidation degree is, more prominent are the hydrogen desorption/adsorption peaks. Two samples of GO (with a oxidation degree of 1:3) were compared and it was possible to conclude that the electrodes produced from Tours' method presented more defined and pronounce hydrogen peaks, compared with the modified Hummers' method, indicating a higher charge density and a higher ECSA.

A MEA for a HT-PEMFC was assembled with an anode based on GO 1:3 (with Hummers') and a commercial electrode at the cathode (Sigracet 10CC). The Nyquist plot shows high ohmic and electrodes resistance. The anode used in the HT-PEMFC was not optimized and the cathode electrode is for LT-PEMFC. All of this lead to a poor performance of the cell. The quantity of phosphoric acid was not optimized at the membrane and electrodes, also contributing to lowering the MEA's performance.

The main objective of the thesis was fulfilled and presents the first step for a deeper study. Platinum catalyst was deposited in graphene and graphene oxide produced from graphite and graphene. The samples were characterized with several techniques, however not all were able to be subjected to the overall analysis due to time constrains.

Therefore, as future applications, all the samples should be subjected to more characterization techniques, providing a complete study. To fully understand the conditions in which graphene could promote a better platinum deposition, the influence of several parameters (like the pH, the reducing agent, the platinum precursor) should be analysed.

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APPENDIX A - THE IMPORTANCE OF PURIFICATION OF THE MATERIAL

The clear necessity of the purification phase in the improved method used was tested in order to know the importance of this step in the overall methodology. To achieve this, two experiments were made: a sample was purified with the protocol referred previously and another wasn't purified at all. This last sample was extracted from the mixture developed before. The fact that the source is the same allows supporting the validity of the results obtained. To compare the results of the purification of the graphite oxide with a non-purified mixture, the non-purified example was placed in in an oven for, approximately, one month. In order to facilitate this process, the sample was covered by an aluminum sheet at a temperature of 40º C.

***Figure A.1** – Different process stages of the unpurified sample treatment.*

The sample was expected to evaporate, leaving only a powder, which consists in oxidized graphite without purification. After a week the mixture was still in liquid form, therefore, the temperature of the oven was raised to 55º C. Waited another 2 weeks and the solution still presented a considerable amount of liquid. The reason for the extended time of evaporation is unknown. The recipient was then put in the oven at 60ºC for 10 days. The temperature was not raised since the effects of higher temperatures on the graphene were unknown. The results were the same, so a different approach was planned. The solution was really dark and with a bigger percentage of liquid, comparing to the solid. Therefore, the liquid was decanted and the solid was removed. All of these parts were placed in the oven at 35ºC and, after two days in the oven, the flasks with liquid solution presented a full sedimentation (dark liquid under and a transparent liquid as supernatant).

This aspect was remarkable since it took a short period of time to achieve this point. The transparent liquid (water, considering the previous stages of work) was decanted and the three flasks were put in a lyophilizer for four days. When these were removed it was possible to discern that the dark compound (in the two flasks referred) was still liquid and the visual results did not present a promising interest.

***Figure A.2** – Clear state separation between the material in test (bottom) and the rest of the solution (supernadant).*

Therefore, after consideration, the flasks were once again left in the lyophilizer for another four days in order to remove the liquid and obtain a good amount of solid, to test it further and understand the importance of purification, according with this new method. When removing the samples, two of them still had liquid, although this time both had a solid layer on the bottom of the container. It is not yet perceptible the main reason of the presence of the referred liquid, but some improvements had been verified. A new lyophilization was performed.

After several months of study, no viable sample was obtained, which reinforce the importance of purification in an oxidation methodology.

***Figure A.3** – Lyophilizer used for all the oxidized samples.*

APPENDIX B - GO MEMBRANES

During this procedure, GO produced from commercial graphene (H5 and M5) could not be filtrated as anticipated, since it was verified that a membrane was starting to form on the top of the filter. As a test, some membranes were developed in order to understand their production and different properties. To appreciate the results the succeeding experiments were established.

***Table A.1** – Conditions used to prepare several GO membranes.*

Sample	1	2	3	4	5	6	7	8
Volume of sample	2 mL	2 mL	3 mL	3 mL	4 mL	4 mL	5 mL	5 mL
Time filtrating	4 min	8 min	4 min	8 min	4 min	8 min	4 min	8 min

It is worth mentioning that the experiments referred were made with GO developed with graphene with a degree of oxidation of 1:6. It was observable that, as expected, the samples with bigger volume presented more consistency and different layers were easily verified. However, the time left filtrating did not affect the properties of the membrane, since it took less than 2 minutes to the membrane achieve its final stage.

By filtrating the GO from graphene 1:3 it was produced one membrane with 5 mL during 8 minutes to future comparisons. More characterization processes are required to fully understand all the properties, like the permeability. These membranes could provide interesting uses in the future (nanofiltration, for example), but more tests were not developed since it wasn't one of the main objectives of the present work.

***Figure A.4** – GO membrane obtained with 5 mL of solution during 8 minutes of filtration.*

APPENDIX C – PROTOCOLS

Oxidation Protocol

Tour's method (1:6):

+ 9:1 mixture of concentrated H2SO4/H3PO4 (360:40 mL) is added to a mixture of graphite flakes (3,0 g – 1 wt equiv) and KMnO4 (18,0 g – 6 wt equiv);

+ The reaction is heated to 50º C and stirred for 12h;

+ The reaction is cooled to room temperature and poured onto DI ice (approximately 400 mL) with 30% H2O2 (3 mL);

+ The mixture is sifted through a metal U.S. Standard testing sieve (W.S. Tyler, 300 μm);

+ The solution is filtered (through polyester fiber);

+ The filtrate is centrifuged (4000 rpm for 4h);

+ The supernatant is decanted;

+ The remaining solid material is washed in succession with 200 mL of water, 200 mL of 30% HCl and 200 mL of ethanol (2x);

+ For each wash the solution is sifted and then filtered (through polyester fiber);

+ The filtrate is centrifuged (4000 rpm for 4h);

+ The supernatant is decanted;

+ The material remaining is coagulated with 200 mL of ether;

+ The resulting suspension is filtered over a PTFE membrane (with a 0,45 μm pore size);

+ The solid obtained on the filter is vacuum-dried overnight at room temperature.

Tour's method that we used on the oxidation of graphite (some changes compared to the one above): Oxidation degree of 1:6

+ 9:1 mixture of concentrated H2SO4/H3PO4 (18:20 mL) is added to a mixture of graphite flakes (1,5 g – 1 wt equiv) and KMnO4 (9 g – 6 wt equiv);

+ The reaction is heated to 50º C and stirred for 15h15;

+ The reaction is cooled, for approximately 1 hour, to room temperature;

+ The mixture is poured onto DI ice (approximately 200 mL) with 30% H2O2 (3,5 mL) while manually stirring;

+ The solution is centrifuged for 1 hour (two times at 4000 rpm for 0,5h each);

+ The supernatant is decanted;

+ The remaining material is washed with 100 mL of DI water;

+ The solution is centrifuged for half hour (4000 rpm for 0,5h);

+ The supernatant is decanted;

+ The remaining material is washed with 100 mL of HCl (32%);

+ The solution is centrifuged for half hour (4000 rpm for 0,5h);

+ The supernatant is decanted;

+ The remaining material is washed with 100 mL of ethanol;

+ The solution is centrifuged for 1 hour (two times at 4000 rpm for 0,5h);

+ The supernatant is decanted;

+ This last wash was repeated and the mixture was centrifuged twice (with the conditions previously refereed) and decanted in the end;

+ The material remaining is coagulated with 100 mL of ether;

+ The solid obtained on the filter is vacuum-dried overnight at 30º C.

Oxidation degree of 1:3

All the process developed with this degree of oxidation is equal to the previous one mentioned, however the quantities of the materials used are different:

+ 9:1 mixture of concentrated H2SO4/H3PO4 (18:20 mL) is added to a mixture of graphite flakes (1,5 g – 1 wt equiv) and KMnO4 (4,5 g – 3 wt equiv);

Protocol for Platinum deposition with EG as reducing agent.

Volumes of solutions used in the platinum deposition:

- 5 mL of water is provided by the NaOH [10 M] solution;

$$NaOH\ (10M)$$

$$n = 10\frac{mol}{L} \times 0{,}100\ L = 1mol$$

$$m = 1 \times 40 = 40\ g$$

$$40\ g\ of\ NaOH\ (pellets)\ dissolved\ in\ 100\ mL\ of\ water$$

- 7,43 mL of a mixture with EG and H2PtCl6 salt;

Is added 0.8 wt.% H2PtCl6.6H2O solution in the EG solution, at room temperature and with agitation.

Since the Platinum deposition planned is 20%, the following calculations must be considered.

$$\frac{x}{100 + x} = 0{,}2 <=> x = 20 + 0{,}2 \times x <=> x = \frac{20}{0{,}8} = 25\ mg$$

$$H2PtCl6 \cdot 6H2O \rightarrow 37{,}5\%\ Pt$$

$$mass\ of\ salt = \frac{25}{0{,}375} = 66{,}67\ mg$$

For 0.8 wt.% H2PtCl6.6H2O, the total volume of the mixture must then be

$$m = \frac{66{,}67}{0{,}008} = 8333{,}3\ mg => m\ (EG) = 8333{,}3 - 66{,}67 = 8266{,}6\ mg = 8{,}2666\ g$$

$$d\ (EG) = 1{,}1132\frac{g}{cm3} => V\ (EG) = \frac{8{,}2666}{1{,}1132} = 7{,}43\ mL$$

- 87,57 mL of EG solution.

$$95\ mL - 7{,}43\ mL = 87{,}57\ mL\ of\ Ethylene\ Glycol$$

Therefore, the total volume of solution added is 100 mL.

Protocol for Cyclic Voltammetry

As mentioned, cyclic voltammetry is one of the most used techniques in electrochemical analysis for the study of electro-active catalytically species and electrode surfaces. According to the present study, the working electrode must be the result from Pt/C, with 20% of platinum deposition, produced earlier. Some commercial samples must also be considered, since they allow to understand, by comparison methods, the quality of the results.

Preparing electrodes:

+ A mixture containing about 0,1 g of Pt/C catalyst powder is added to a 1-4 mL of isopropyl alcohol;
+ The mixture is then sonicated for 15 min;
+ The GDL is weighted;
+ A volume of 100-200 µL of the solution is sprayed on commercial Sigracet GDL (SGL Carbon, ref.:GDL 24 BC);
+ The mixture is weighted;
+ The combination is left drying at room temperature overnight;
+ The material e weighted and ready to be used.

System assembly:

+ A solution of 1M of H2SO4, with a volume of 1L, is prepared;

M(H2SO4) = 98,08 g/mol | d(H2SO4) = 1,84 g/cm3

$$V = \frac{98}{1{,}84} = 53{,}3\ mL$$

Assuming a 95% concentrated H2SO4 solution as a reactant, than the mixture is produced as follow

$$V = \frac{53{,}3}{0{,}95} = 56{,}1\ mL\ of\ H_2SO_4$$

Since the entire solution has a volume of 1 L, then 56,1 mL of H2SO4 is added to 943,9 mL of distilled water.

NOTE: For safety reasons, water is never added to a concentrated acid. Only the reverse may occur.

How to prepare the H2SO4 1M solution:

+ Place 943,9 mL of distilled water into an 1L Erlenmayer;
+ Add, drop-by-drop, 56,1 mL of H2SO4 (95%) to the water, with low agitation;
+ Leave agitating at 100 rpm for several more minutes;
+ Stop the agitation and let the solution rest for a while;
+ Store the mixture.

+ An inert gas (Nitrogen, for example) is used to bubble the solution, in order to remove the oxygen, with a stream of 100 mL/min for 1 hour.

+ Meanwhile, the electrodes are assembled and all the system is established.

+ Three-electrode system (1 cm2 each) is placed in the acidic solution, at room temperature;

- SCE reference electrode of Ag/AgCl;
- Pt mesh as counter electrode;
- Working electrode with the catalyst.

+ An inert gas (usually N_2) is bubbling in the electrolyte, during the testing phase.